

TENT COOPERATION TRE, /

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 16 May 2000 (16.05.00)	
International application No. PCT/GB99/02757	Applicant's or agent's file reference P019832WO
International filing date (day/month/year) 19 August 1999 (19.08.99)	Priority date (day/month/year) 03 September 1998 (03.09.98)
Applicant WILLIAMS, David, Edward et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
31 March 2000 (31.03.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Pascal Piriou Telephone No.: (41-22) 338.83.38
--	--

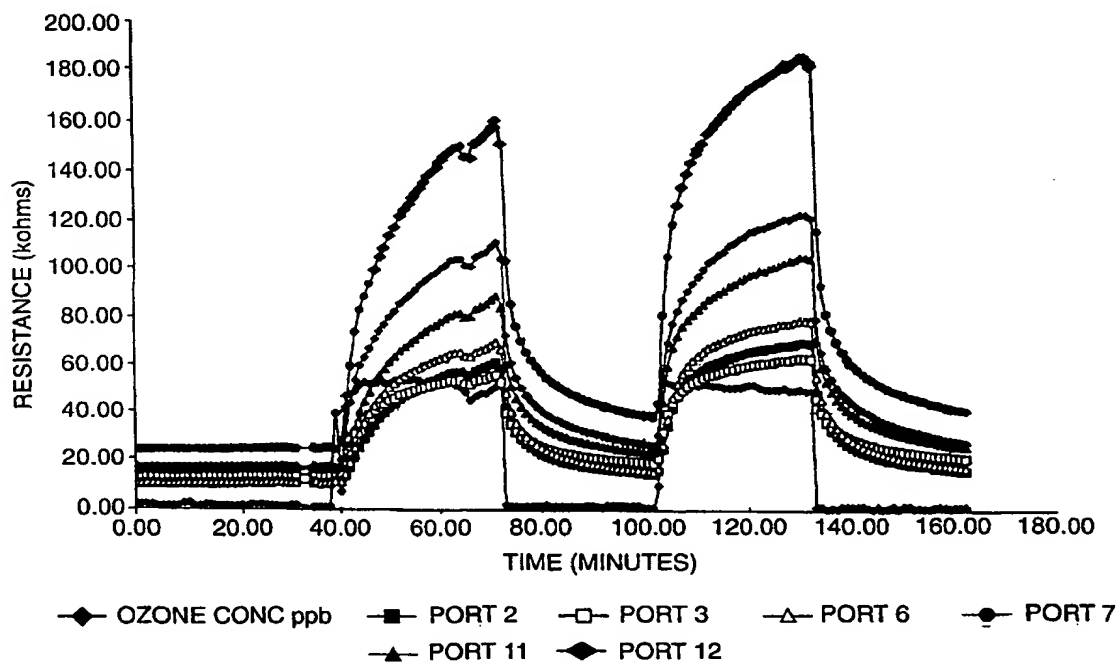
PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : G01N 33/00, 27/12		A1	(11) International Publication Number: WO 00/14531
			(43) International Publication Date: 16 March 2000 (16.03.00)
(21) International Application Number: PCT/GB99/02757			(81) Designated States: CA, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
(22) International Filing Date: 19 August 1999 (19.08.99)			
(30) Priority Data: 9819228.9 3 September 1998 (03.09.98) GB			
(71) Applicant (for all designated States except US): CAPTEUR SENSORS AND ANALYSERS LIMITED [GB/GB]; 11 Moorbrook Park, Didcot OX11 7HP (GB).			
(72) Inventors; and (75) Inventors/Applicants (for US only): WILLIAMS, David, Edward [GB/GB]; 41 Oxford Road, Abingdon OX14 2EE (GB). PRATT, Keith, Francis, Edwin [GB/GB]; 22 Roebuck Court, Didcot OX11 8UT (GB). JONES, Roderic, Lewis [GB/GB]; 7 Bandon Road, Girton, Cambridge CB3 0LU (GB). COX, Richard, Anthony [GB/GB]; 4 College Farm Court, High Street, Barton, Cambridge CB3 7AL (GB).			
(74) Agent: COLGAN, Stephen, James; Carpmaels & Ransford, 43 Bloomsbury Square, London WC1A 2RA (GB).			

Published*With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: SEMICONDUCTOR GAS SENSING



(57) Abstract

The concentration of oxidising gases such as NO₂, NO, Cl₂, O₃ in a gas mixture is determined by perturbing the operating conditions of a semiconductor gas sensor; the perturbation may be a temperature change or a change in concentration of the gas; the invention is particularly suited to ozone sensing with tungstic oxide sensors.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

SEMICONDUCTOR GAS SENSING

This invention relates to the semiconductor gas sensing of oxidising gases such as nitrous and nitric oxide, chlorine, and ozone.

In the following description the invention will be exemplified with reference to ozone sensing, but the general principles are applicable to other oxidising gases. Parts per billion (ppb) quoted hereinafter are by volume.

In our previous application WO-95/35495, we described a method of measurement of ozone concentration involving the measurement of electrical resistance of a porous tungstic oxide element, held at elevated temperature (200-500°C). When the element is held at constant temperature, the sensitivity to ozone tends to vary with time and to be dependent upon the history of the device, including previous exposure to ozone. Other semiconducting oxides have been shown to exhibit resistance increases at elevated temperature in the presence of small concentrations of ozone in the air: In_2O_3 , pure and variously doped, by Takada et al, Sensors & Actuators B : Chemical 13 (1993) 404; MoO_3 by Garlo et al., Sensors & Actuators B : Chemical 47 (1998) 92. We have now discovered that SnO_2 also shows the effect (see Figure 1), though at rather lower temperature (~200°C) and with problems of baseline stability. We believe that the phenomenon is generic to a certain general class of semiconducting oxides for which oxygen vacancies can be created at the surface, at the operating temperature, in air, in sufficient concentration to substantially affect the concentration of electronic charge carriers and hence the electrical conductivity.

The invention is defined by the claims hereinafter.

We have discovered a set of methods for analysis of ozone concentration in air, which are generally applicable to the afore-mentioned class of oxides. The methods surprisingly result in (1) a significant increase in the stability of the signals generated by sensors incorporating these materials, and (2) significantly reduce the lower detection limit of the sensors for ozone to concentrations of a

few ppb, which is typical of the UV ozone analysers conventionally employed to detect this molecule. These methods involve causing a perturbation of the condition of the sensor and analysing the resulting time variation of the sensor resistance or conductance. These methods are:

- 5 (1) a perturbation of the sensor temperature, which may be small or large, in the form of a square pulse or a sinusoidal variation,
- (2) a perturbation of the ozone concentration near the sensor, either by periodically switching the gas flow to the sensor through a catalyst bed which destroys any ozone present, or by simply altering the flow rate of gas over the
10 sensor, using the hot sensor itself to cause local decomposition of the ozone present in the air.

The methods give substantially increased accuracy and stability, and consequently a greater reliability of measurement, especially at very low ozone concentration (less than 100 ppb in air). A very low detection limit for ozone can
15 be achieved, which can be reliably sustained in measurement over a long period of time. A typical detection limit achieved using a device based on WO_3 is 2.5 ppb in air, reliably sustained without change of calibration over at least 3 months.

Preferred features of the invention will now be described, by way of
20 example, with reference to the accompanying drawings, in which:

Figure 1 is a graph showing the response of an SnO_2 sensor operated at 175°C to a pulse of 50 ppb ozone in air,

Figure 2 is a graph showing the response of a WO_3 sensor to 50 ppb ozone in air after having been stepped to 600°C from an operating temperature
25 of 400°C,

Figures 3 and 4 show the variations in time constants of equation (1) hereinafter with ozone concentration,

Figure 5 shows the variation in resistance of the WO_3 sensor to ozone concentration and the result of curve fitting applied thereto,

Figure 6 shows the response of the WO_3 sensor to ozone concentration over a period of days,

Figure 7 is a graph illustrating the time required to reset the sensor surface as a function of reset temperature,

5 Figure 8 is a graph illustrating the energy consumed in resetting the sensor surface, as a function of reset temperature,

Figure 9 compares the results of employing a WO_3 sensor according to the invention to monitor street level ozone concentration as compared to similar results obtained with a conventional UV absorption instrument,

10 Figure 10 compares the results of employing a WO_3 sensor according to the invention to provide a vertical profile of ozone in the atmosphere as compared to similar results obtained with a conventional instrument,

Figure 11 shows the response of a number of WO_3 sensors operated according to the invention when subjected to pulses of ozone, and

15 Figure 12 shows the effect of air flow rate on a WO_3 sensor operated according to the invention.

The invention employs different methods to perturb the sensor and to analyse the results, as will now be described.

20 Method 1: - step to a high temperature to reset the surface
 - step back to a low temperature to make the measurement
 - analyse the variation of resistance with time at the low
 temperature to obtain the ozone concentration
 - repeat the sequence.

25 For example with a device based on WO_3 , the "high" temperature can be 400°C - 800°C and the "low" temperature can be 200°C - 500°C , with the obvious constraint that the "high" temperature should be greater than the "low" temperature.

Figure 2 shows an example of this. In the presence of ozone in the air,

the device temperature was stepped to 600°C for 300s, then stepped back to 400°C for 300s. The time-variation of resistance at 400°C following the step back ($t=0$) is shown. The conductivity, S (reciprocal of resistance) at the low temperature shows the following variation:

$$S(t) = S_{lim} + a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (1)$$

where

$$S_{lim} = S_{\infty} + b_o/(O_3)$$

$$\tau_1 = b_1/(O_3)$$

$$\tau_2 = b_2/(O_3)$$

where (O_3) denotes the ozone concentration.

Here, S_{∞} , a_i are constants which depend on the time and temperature of the "high" temperature step. The b_i depend upon the temperature of the "low" temperature step, at which the measurement is made but do not depend on the high temperature step values. Typically, $b_2 \approx 10b_1$, so that the second time-dependent term is only significant at higher ozone concentration. If the measurement temperature (the "low" temperature) is decreased then the ratio b_2/b_1 increases, so again the second time-dependent term becomes less significant.

Application of method to ozone measurement

(a) by curve-fitting the data to equation (1), the values of τ_1 , τ_2 are determined. By reference to a calibration curve of τ_1 (and if necessary τ_2) against ozone concentration, the ozone concentration is obtained. The sensor and the stability of the operating circuitry are checked by checking the stability of the parameters S_{∞} , a_1 , a_2 , which are also obtained from the fit. If the measurement time is limited, or the ozone concentration is low enough, or the measurement temperature is low enough, then only one time constant will be required to describe the data, and the reliability of the parameter fit can be improved.

In the example shown in Figure 2, the fitted curve provided the values τ_1

= 30s (seconds) and τ_2 - 130s. Examples of the variation of time constants with ozone concentration are shown in Figures 3 and 4. In Figure 4, the fitted line corresponded to

$$\tau/s = (1300 \pm 70)/(O_3 \text{ppb})$$

5 Figure 5 shows the variation of sensor resistance to ozone concentration and fitting the equation

$$1/R = a + b/O_3$$

to the results. In the example shown

$$a = 1.81 \cdot 10^{-7} \Omega^{-1}$$

10
$$b = 2.44 \cdot 10^{-5} \Omega^{-1} \cdot \text{ppb}$$

(b) the resistance or conductance at a particular time after the change of temperature can be determined, and the ozone concentration can be obtained from a calibration curve of this resistance against ozone concentration.

Manipulation of equation (1) shows that a linear calibration of either
 15 conductance or resistance will be obtained if the time constants τ_1, τ_2 are sufficiently long: i.e. at low $[O_3]$. Figure 6 shows an example. In this example, between the calibration runs, the sensor had been used continuously, measuring ozone in urban air. The calibration did not drift over a period of some months. From the calibration line, a detection limit of 2.5 ppb is deduced.

20 In Figure 6, the ordinate "Response" is $R_g/R_o - 1$, where R_g is the resistance of the sensor in the presence of ozone and R_o is the resistance in the presence of air. The response values were taken at 128s, with all data having a relative humidity of 49%. The data can be fitted to a straight line

$$\text{Response} = A + B \cdot [O_3]$$

25 In the example shown in Figure 6

$$A = -0.192 \text{ with a standard deviation of } 0.083$$

$$B = 0.045 \text{ with a standard deviation of } 0.002.$$

Unlike (a), this method requires the parameters S_∞, a_1, a_2 to remain stable that is, that the surface should be fully "reset". We have found that this

can be achieved by an appropriate choice of temperature and time for the "high" temperature step. For Figure 6, it was 600°C and 300s, with measurement at 400°C. Figure 7 shows the required time (for reset) as a function of the temperature, for WO₃-based devices. The higher the temperature, the shorter the time. Figure 8 shows the energy consumption during the high temperature step (power required x time required). The energy consumption decreases with increasing reset temperature. So, the higher the reset temperature the better, both for time resolution (the device is not measuring during the reset period) and for energy consumption (the less energy consumed the better for applications requiring battery power, e.g. balloon-borne instruments).

(c) the time, t^* required to achieve a particular resistance, R^* , can be measured and the ozone concentration derived from a calibration derived from a calibration curve. From equation (1), t^* varies approximately as $1/(O_3)$. The value, R^* , is chosen according to the expected ozone concentration: obviously, choosing a lower value will decrease t^* for a given (O_3). This method has the advantage of measurement simplicity: a counter is started at the end of the reset pulse and stopped when a comparator circuit senses that the measuring current through the sensor falls below a preset level.

(d) is a combination of (b) and (c). The resistance is monitored as a function of time until the end of a preset measurement time, t_m . A resistance trigger level, R^* , is also set. If, during t_m , the resistance exceeds R^* , then the time of this occurrence, t^* , determines the ozone concentration, the sensor is reset and the sequence repeats. If, at the end of t_m , $R_m < R^*$, then the value of resistance R_m at t_m is used to determine the ozone concentration, the sensor is reset and the sequence repeats. This method gives a wide dynamic range and good response time with simple electronics.

The validity of the results of the two step temperature technique are shown in Figures 9 and 10. In Figure 9 the variation in street level ozone concentration over a period of four days was measured with a WO₃ sensor as

well as with a conventional UV absorption instrument. The two types of measurements agree generally quite well.

Figure 10 shows the results of vertical profiling for ozone in the atmosphere using a WO_3 sensor given a single high temperature reset pulse, and the equivalent results from a conventional ECC ozone sonde. Again, the results agree generally well.

Method 2

- oscillate the temperature by a relatively small amount e.g. $\pm 50^\circ\text{C}$
- either a square-wave oscillation between two temperatures separated by a small amount (e.g. 50°C), with a period of typically 1-10 min, or a sinusoidal oscillation with a period of typically 1-10min
- measure the phase shift (delay time) between temperature oscillation and resistance oscillation and determine ozone concentration from a calibration curve.

In this method, there will, of course, be an oscillation of resistance caused by the effect of temperature on the resistivity of the material (resistance decreases with increasing temperature). This element of the oscillating resistance will have only a small delay time (typically $\sim 0.2\text{s}$) determined by the thermal response time of the sensor. Superimposed upon this will be an additional oscillation due to the effect of ozone. The two effects can be separated using a time-gated measurement scheme. Alternatively, the device can be configured as a multi-electrode device of the type we have previously described in EP-B-591240. If such a device having two electrode spacings is arranged in a bridge circuit, then the output signal will be proportional to the ratio of the two resistances. This resistance ratio will be independent of temperature in the absence of ozone, but, because ozone is a reactive gas which shows a concentration gradient through the sensor layer, the resistance ratio will vary if ozone is present, dependent upon both time and temperature.

Now, consider the resistance oscillation due to the presence of ozone, for the case of a square-wave oscillation of temperature. Equation (1) gives the conductance as a function of time at each of the two temperatures. Because, in this method, the sensor surface is not periodically being completely reset by a step to high temperature, the parameters S_{∞} and a_j may vary with time, dependent on the history of the device and the ozone concentration. However, the parameters b_j do not so vary. Thus the time constants τ_j depend only on the temperature and on the ozone concentration. The method therefore comprises the following steps:

- (1) subtracting the instantaneous change of resistance following each temperature step
- (2) determining the amplitude of the remaining temperature oscillation, from which the ozone concentration may be determined, by reference to a calibration curve
- (3) determining the time constants for each of the two temperatures, according to equation (1), either by curve-fitting equation (1) or by calculation from the resistance values at two or more times during each period of constant temperature
- (4) deriving two further estimates of ozone concentration by reference to calibration curves for the two temperatures.

The method may be generalised to other waveforms for the temperature perturbation, e.g. sinusoidal, using the process of first filtering to remove the instantaneous resistance change caused by the change of temperature and then harmonic analysis, time-correlation function calculation or Fourier transformation to obtain the amplitudes and time constants associated with the ozone-dependent signal, then comparison with calibration curves to derive the ozone concentration.

Method 3 - switch the air stream periodically through a suitable ozone decomposition catalyst

- analyse the resistance variation of the sensor when the ozone is reapplied.

This method is simple to implement using switching valves.

5 The sensor signal when the ozone-destruction catalyst is switched out of the air stream follows equation (1). Figure 11 shows a typical response to a sequence of two pulses of ozone interspersed with ozone-free air, with a number of sensors at constant temperature. The increase of signal amplitude with total ozone dose is a characteristic of these devices when measured at constant temperature, as is the variation between devices. However, the time
10 variation of the signal can be fitted to equation (1). The time constants so derived do not vary from one pulse to another, or from one device to another, wherein reasonable experimental error and the ozone concentration can be determined from the time constants, by reference to a calibration curve. As with
15 the temperature-switching method, this method does not require the sensor resistance to stabilise in order that the ozone concentration be accurately determined.

The results from Figure 11 were for a number of WO_3 sensors powered for 5 days at 400, 500 and 600°C, left unpowered for 30 minutes, and then the two pulses of ozone (50 ppb) applied with measurement made at 500°C. The
20 results from Figure 11 gave time constants $\tau_1 = 77 \pm 21\text{s}$ and $\tau_2 = 520 \pm 61\text{s}$.

Method 4 - periodically greatly reduce the airflow rate over the sensor, then increase it again, with the sensor at constant temperature.
- analyse the time variation of the signal following the increase of flow rate.

25 This method works because ozone is decomposed within the thermal boundary layer near the sensor. The variation of signal with airflow rate normal to the sensor is shown in Figure 12. In Figure 12, the results are for a WO_3 sensor at 400°C exposed to 50 ppb ozone. As for flow rate, 1 Lmin^{-1} equates to about 20 cm.s^{-1} flow velocity normal to the sensor. At sufficiently high flow rate,

the signal achieves a plateau, because ozone is transported to the surface at a rate sufficiently greater than the rate of thermal decomposition near the sensor. At lower flow rate, the signal falls reflecting the fall in ozone concentration near the sensor. At low enough flow rate, the sensor signal is virtually zero.

5 Therefore, if the air flow to the sensor is greatly reduced, (cutting off the flow completely is, of course, one option) then the sensor resistance will relax towards the value characteristic of a zero ozone concentration. Just as in method 3, it is not necessary to attain an exact zero, however. When the flow rate is increased again, to a value on the plateau of Figure 12, the sensor
10 resistance will increase with time, following equation (1). Curve-fitting equation (1), or calculation from two or more points gives the time constants. By reference to a calibration curve, the time constants give the ozone concentration. The other parameters of equation (1) can be used to diagnose continued reliable operation of the sensor.

15 The power drawn by the sensor device will depend on the air flow rate. Therefore, monitoring the sensor power consumption serves two purposes:

(a) it checks that the required flow rate is indeed being delivered and hence diagnoses failure of any of the other components of the system or blockage of the pipe work;

20 (b) it provides a trigger signal to actuate the resistance measurement circuits at the correct time, thus compensating for delays in the flow lines.

CLAIMS;-

1. A method of sensing the concentration of an oxidising gas in a gas mixture using a semiconductor gas sensor having a resistivity sensitive to the oxidising gas, which comprises perturbing the sensor operating temperature and
5 analysing the resultant resistance of the sensor following perturbation.
2. A method according to claim 1, in which the perturbation is a square wave pulse or is sinusoidal.
3. A method according to claim 1 or 2 in which the perturbation comprises increasing the sensor temperature followed by a temperature reduction at which
10 the resistance is analysed.
4. A method according to claim 3 wherein the increased sensor temperature is 400 to 800°C and the reduced temperature is 200 to 500°C.
5. A method according to any preceding claim wherein the sensor resistance is analysed as a function of time.
- 15 6. A method of sensing the concentration of an oxidising gas in a gas mixture using a semiconducting gas sensor having a resistivity sensitive to the oxidising gas, which comprises perturbing the oxidising gas concentration over the sensor and analysing the resultant resistance of the sensor following perturbation.
7. A method according to claim 6 wherein the perturbation comprises reducing
20 the oxidising gas concentration to zero or periodically changing the flow rate of gas over the sensor.
8. A method according to any preceding claim in which the sensor is a semiconductor oxide for which oxygen vacancies can be created at the sensor surface, at the operating temperature, in air, in sufficient concentration to affect
25 substantially the concentration of electronic charge carriers and hence the resistivity.
9. A method according to claim 8 in which the sensor is WO_3 , In_2O_3 , MoO_3 or SnO_2 .
10. A method according to any preceding claim in which the oxidising gas is

NO₂, NO, Cl₂, or O₃.

11. A method according to claim 10 wherein the gas is O₃ and the sensor is WO₃.

12. An apparatus for conducting the method of any of claims 1 to 11.

1/10

FIG. 1

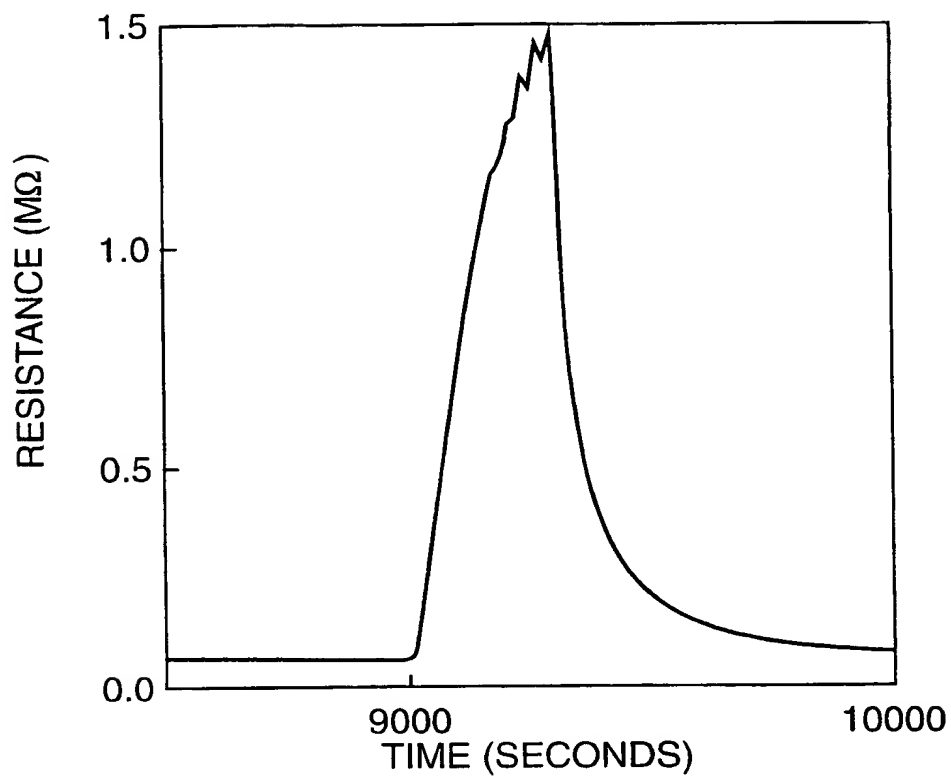
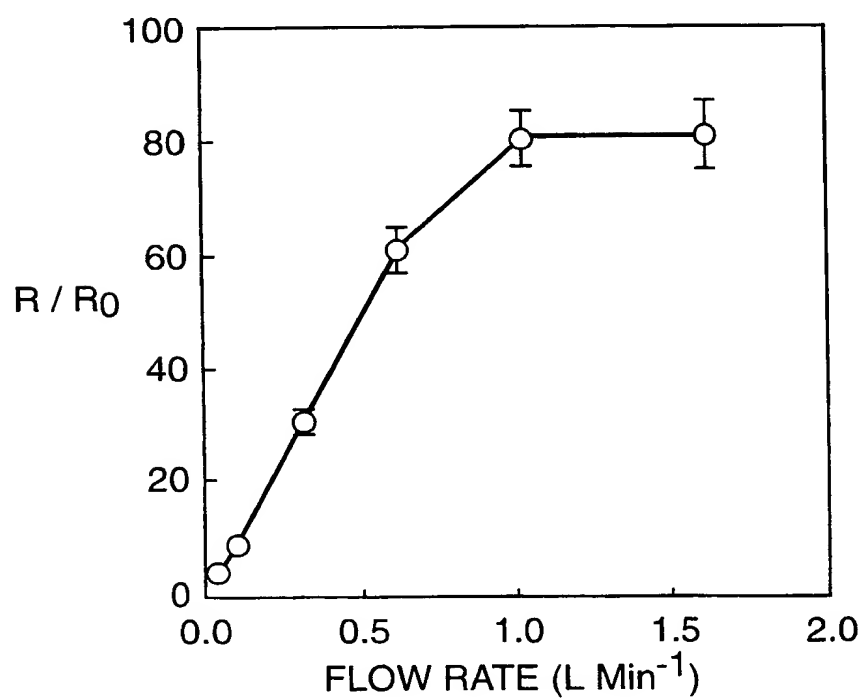
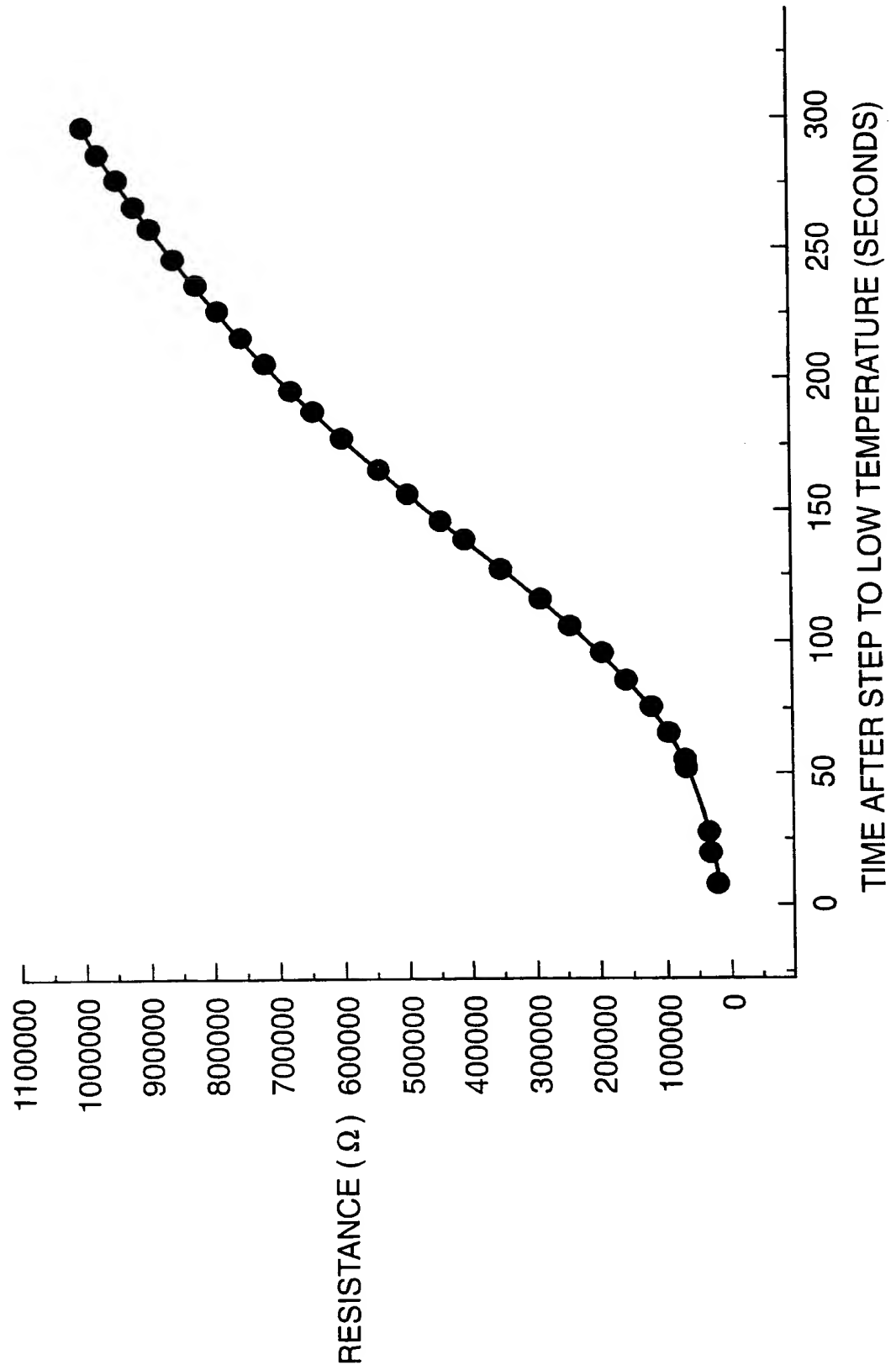


FIG. 12

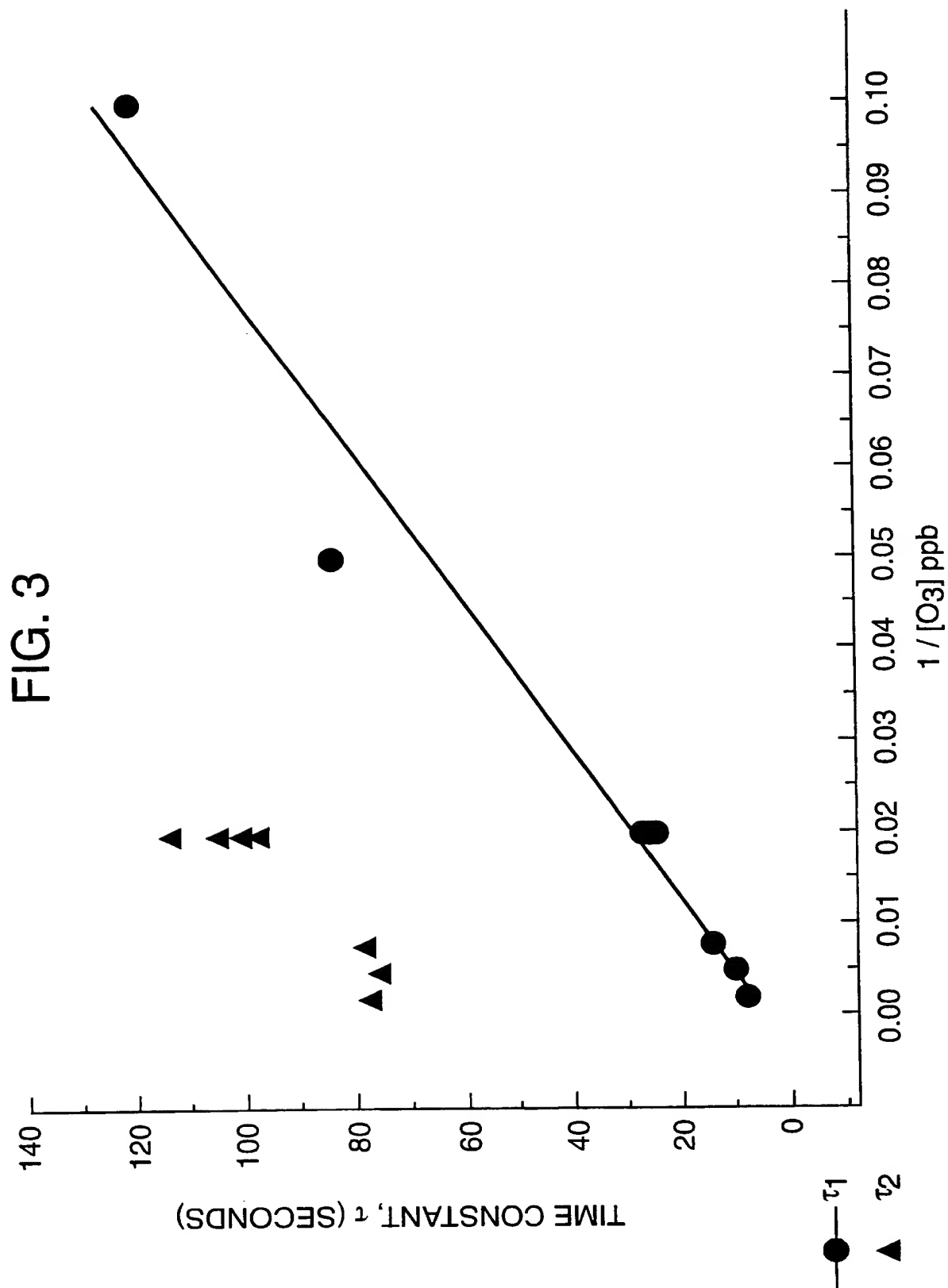


2/10

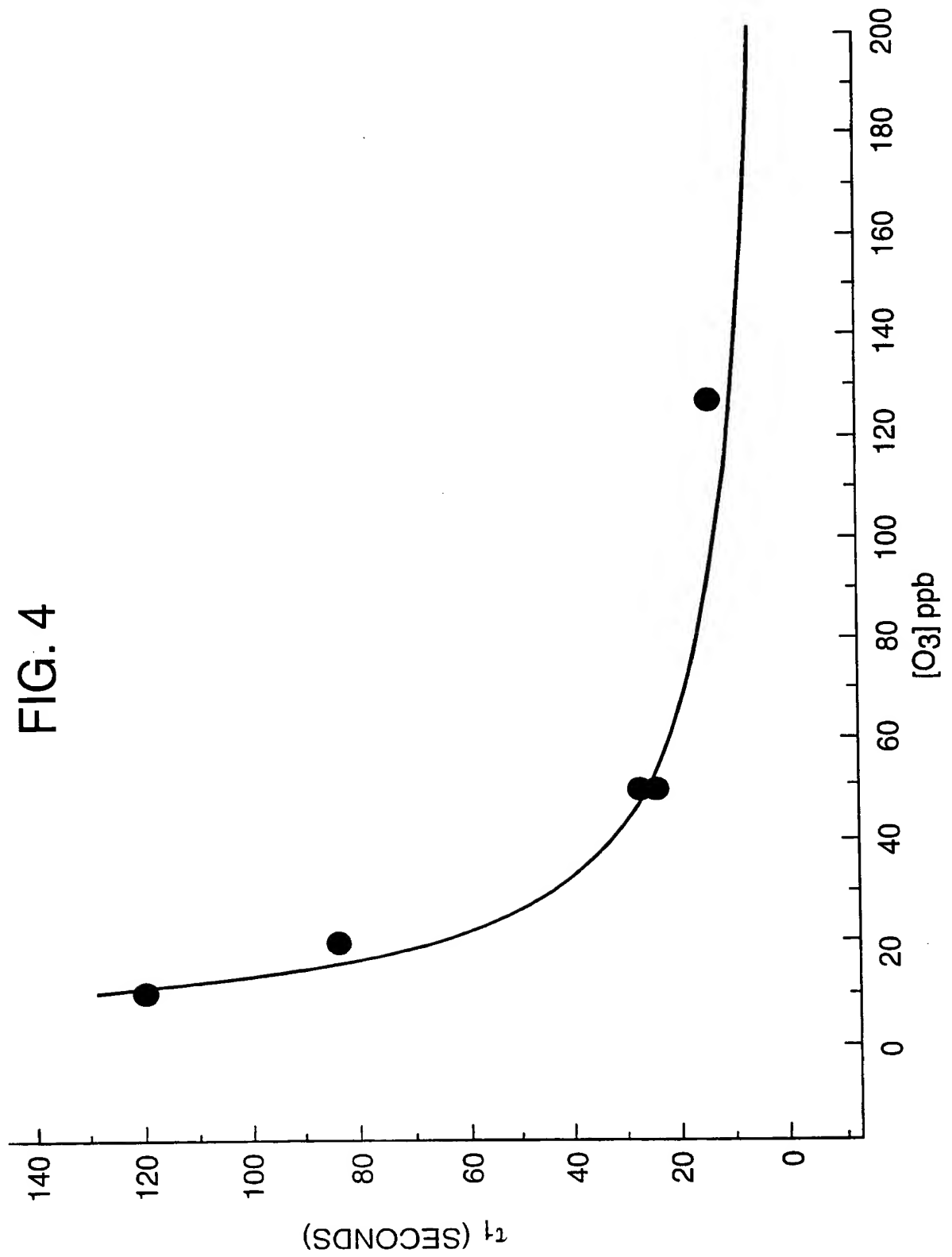
FIG. 2



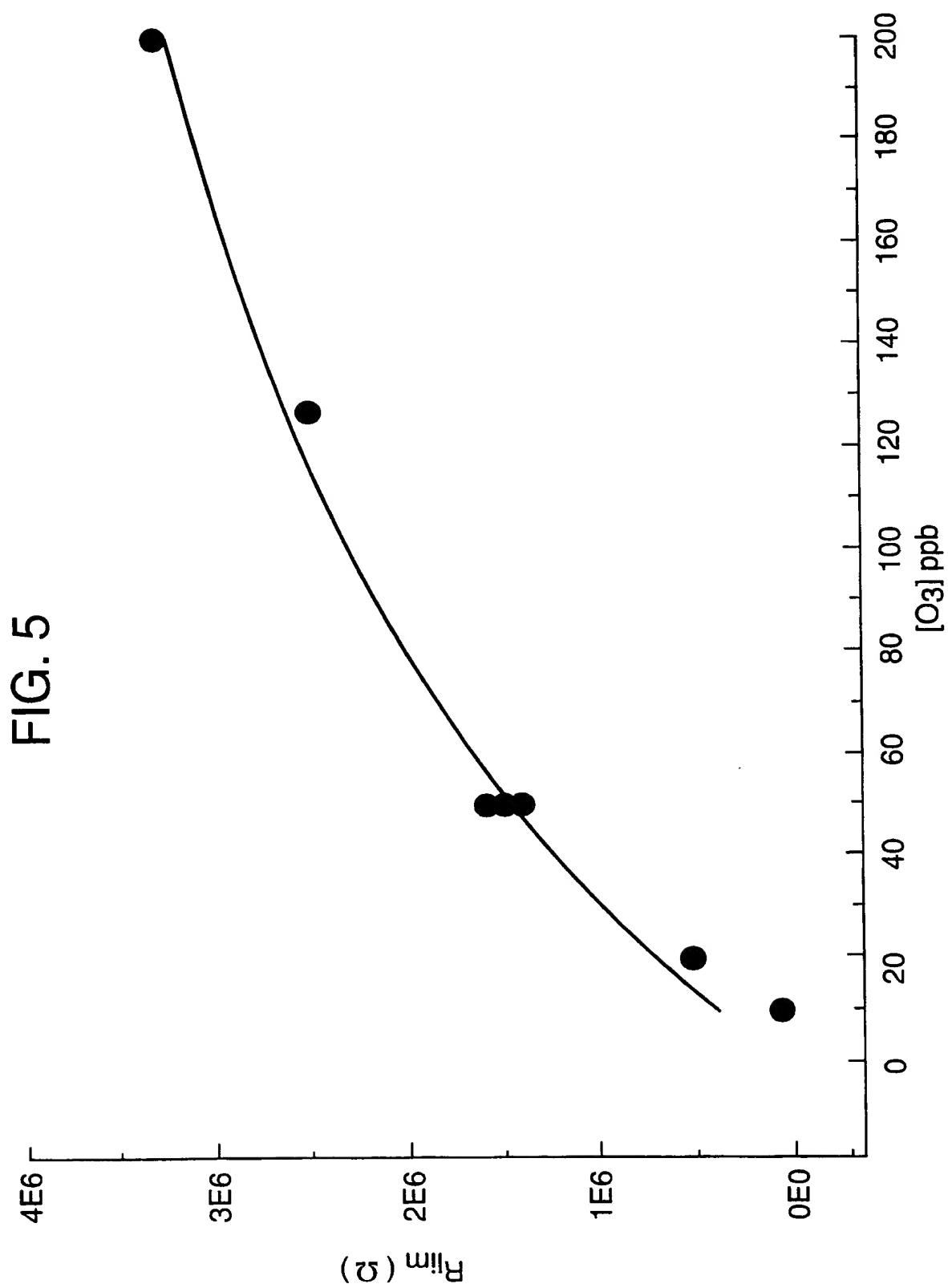
3/10



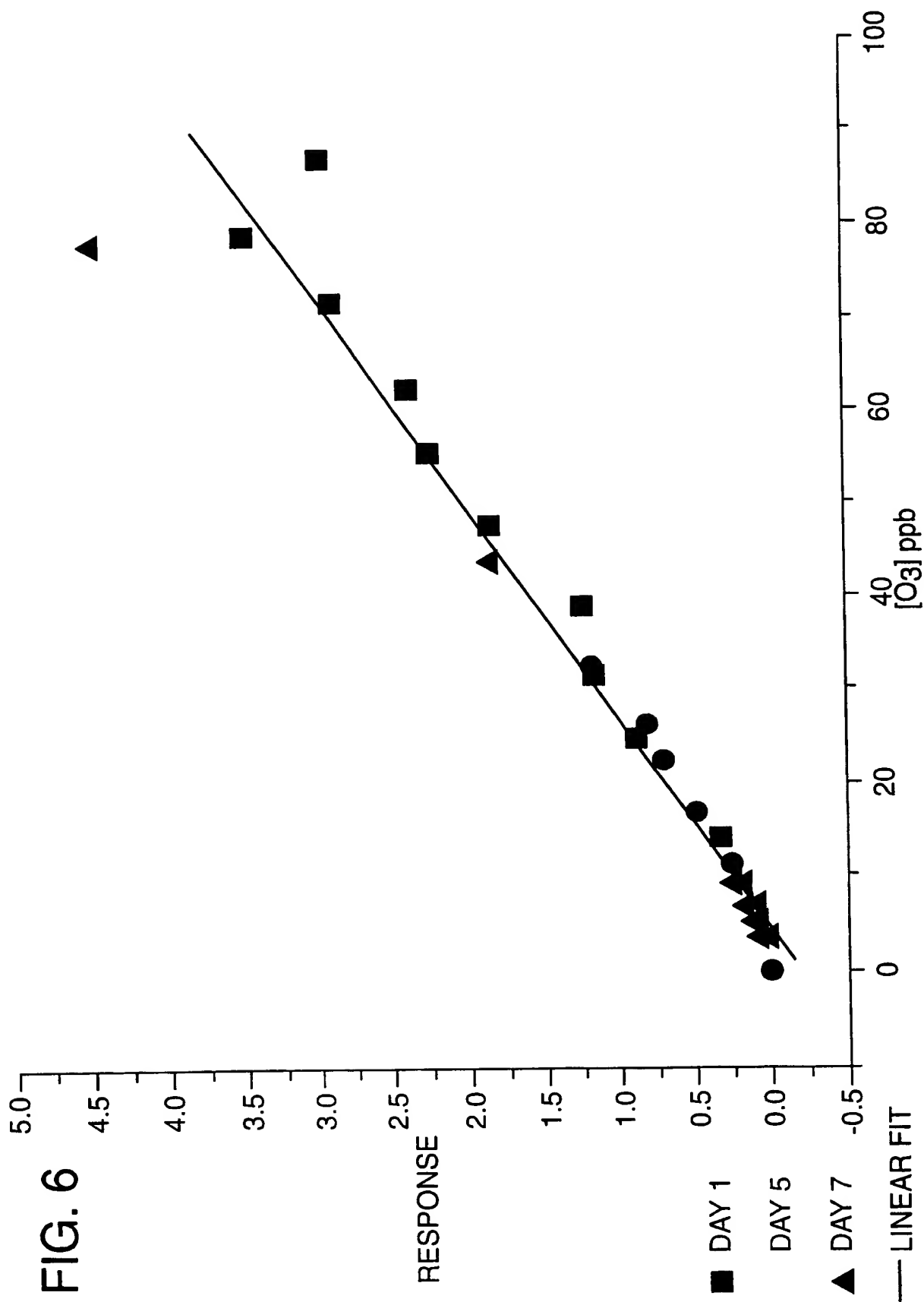
4/10



5/10



6/10



7/10

FIG. 7

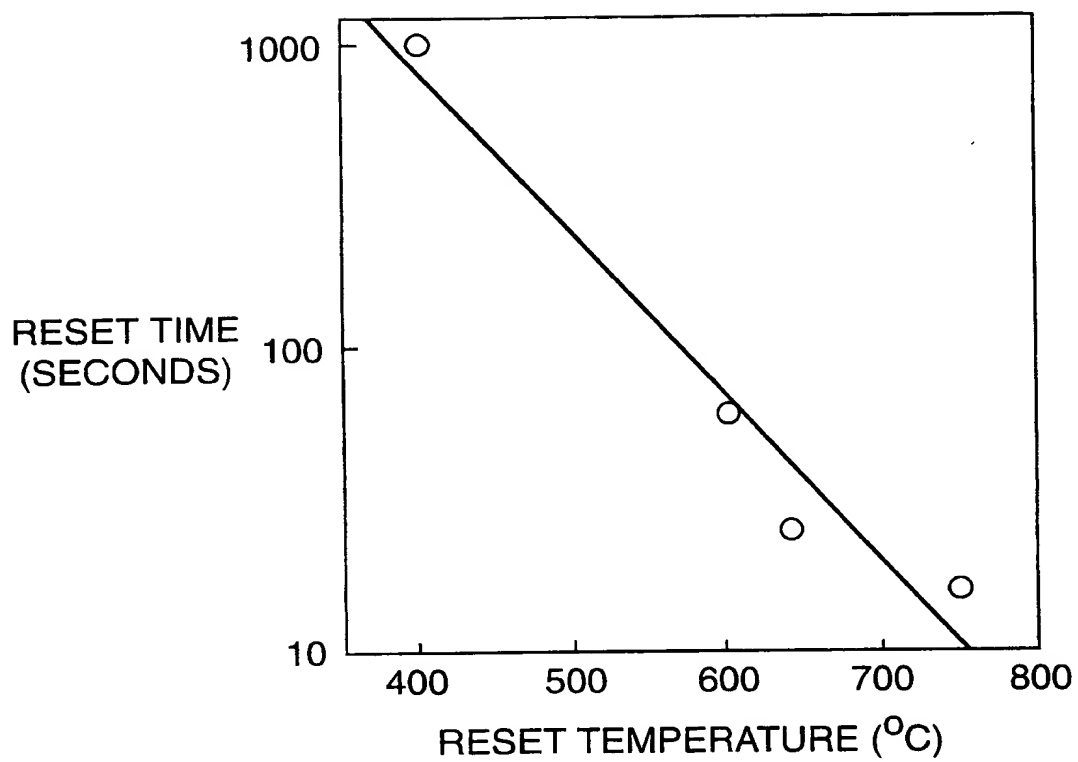
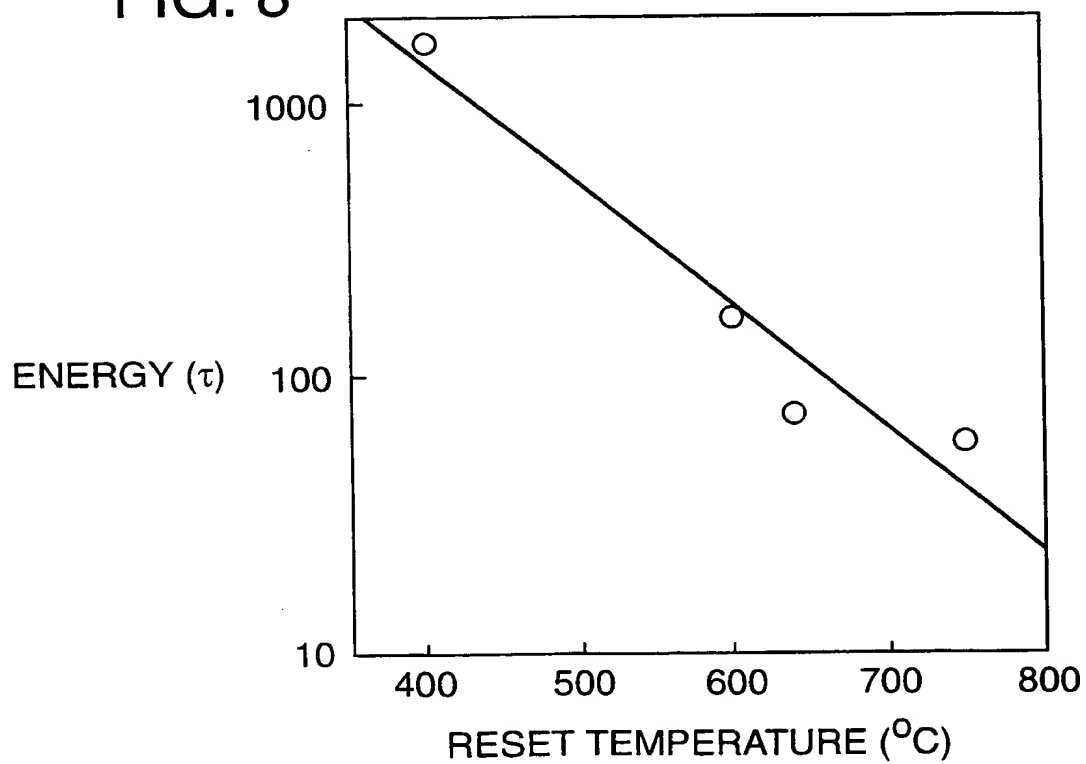
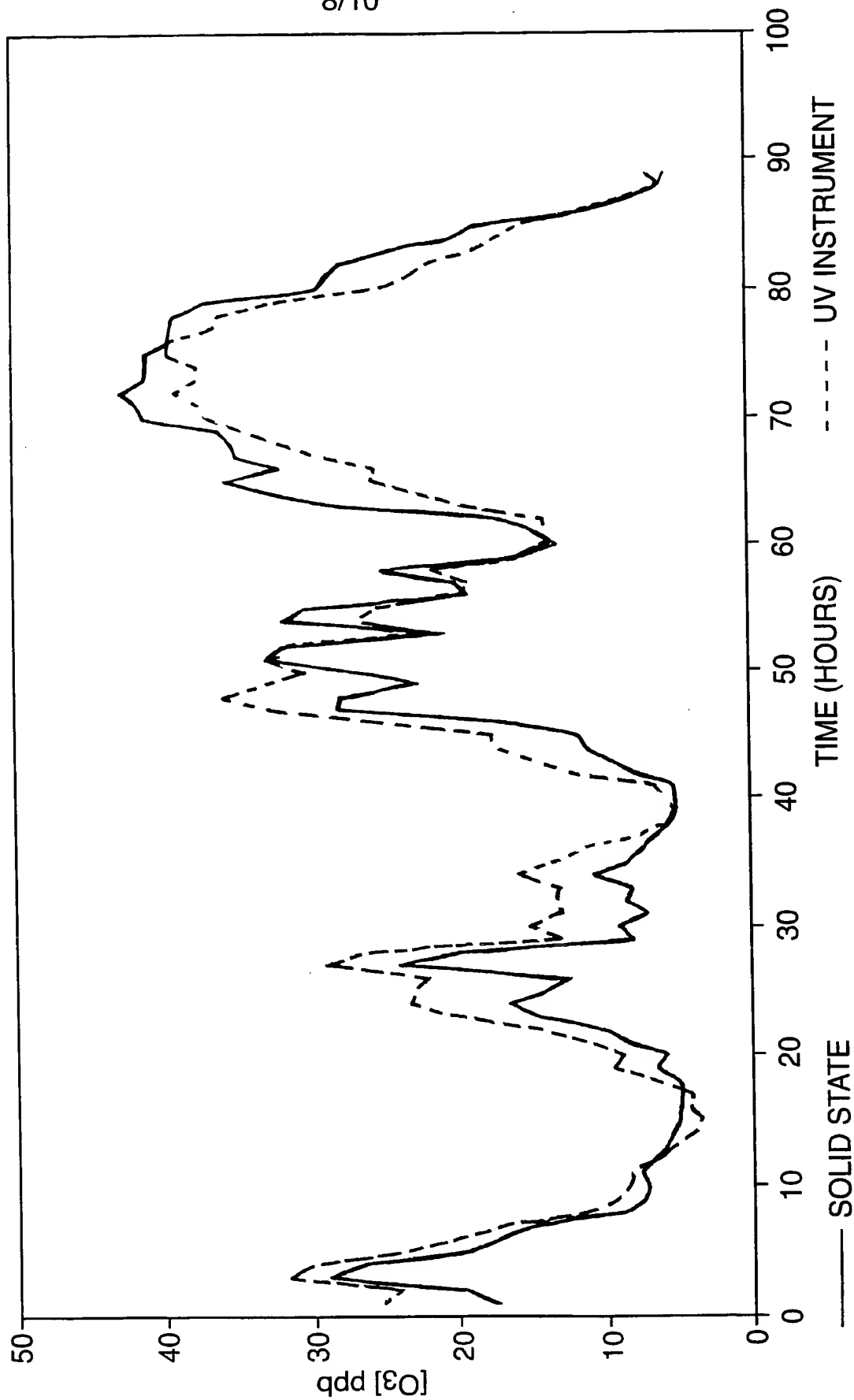


FIG. 8



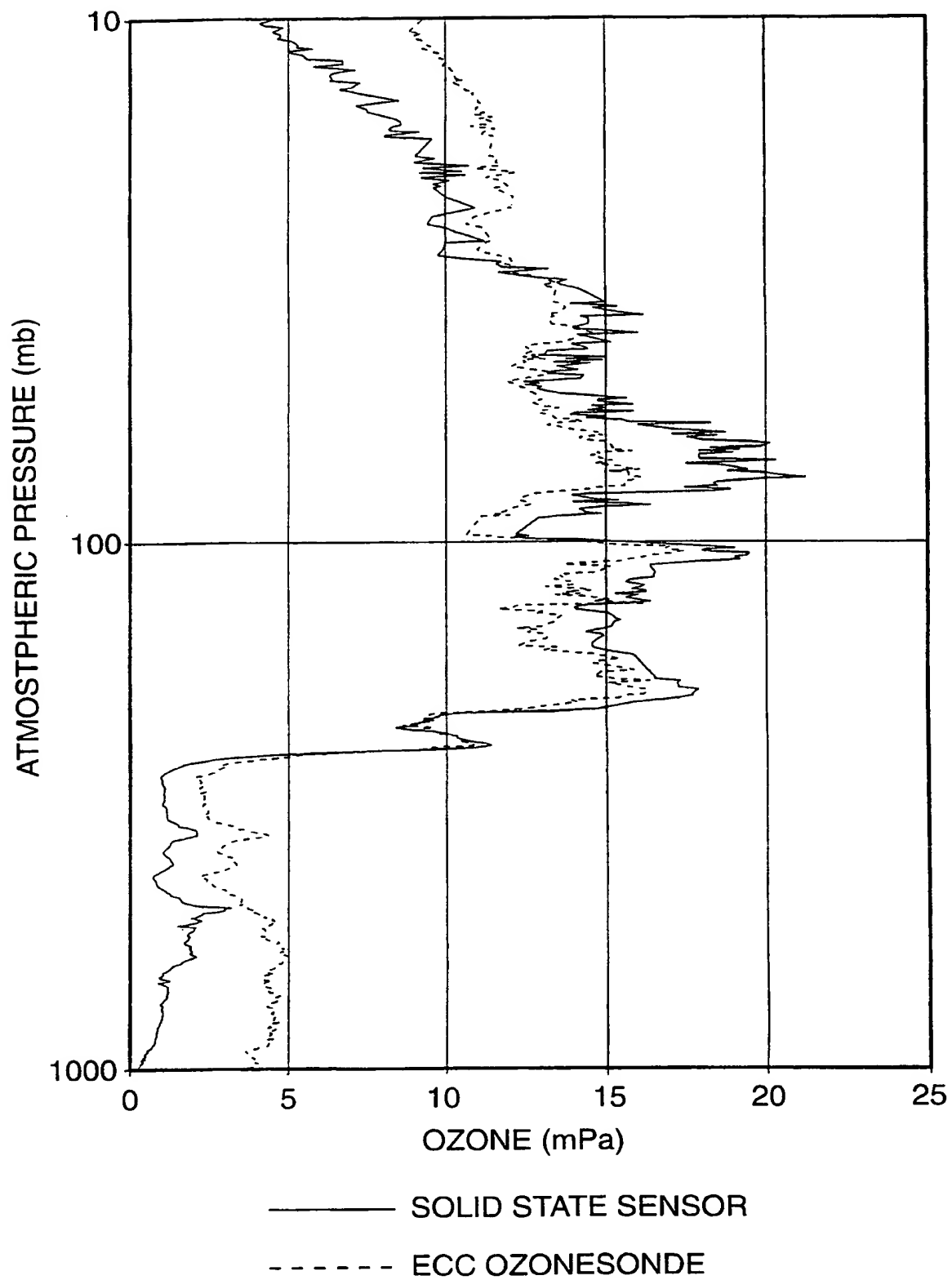
8/10

FIG. 9



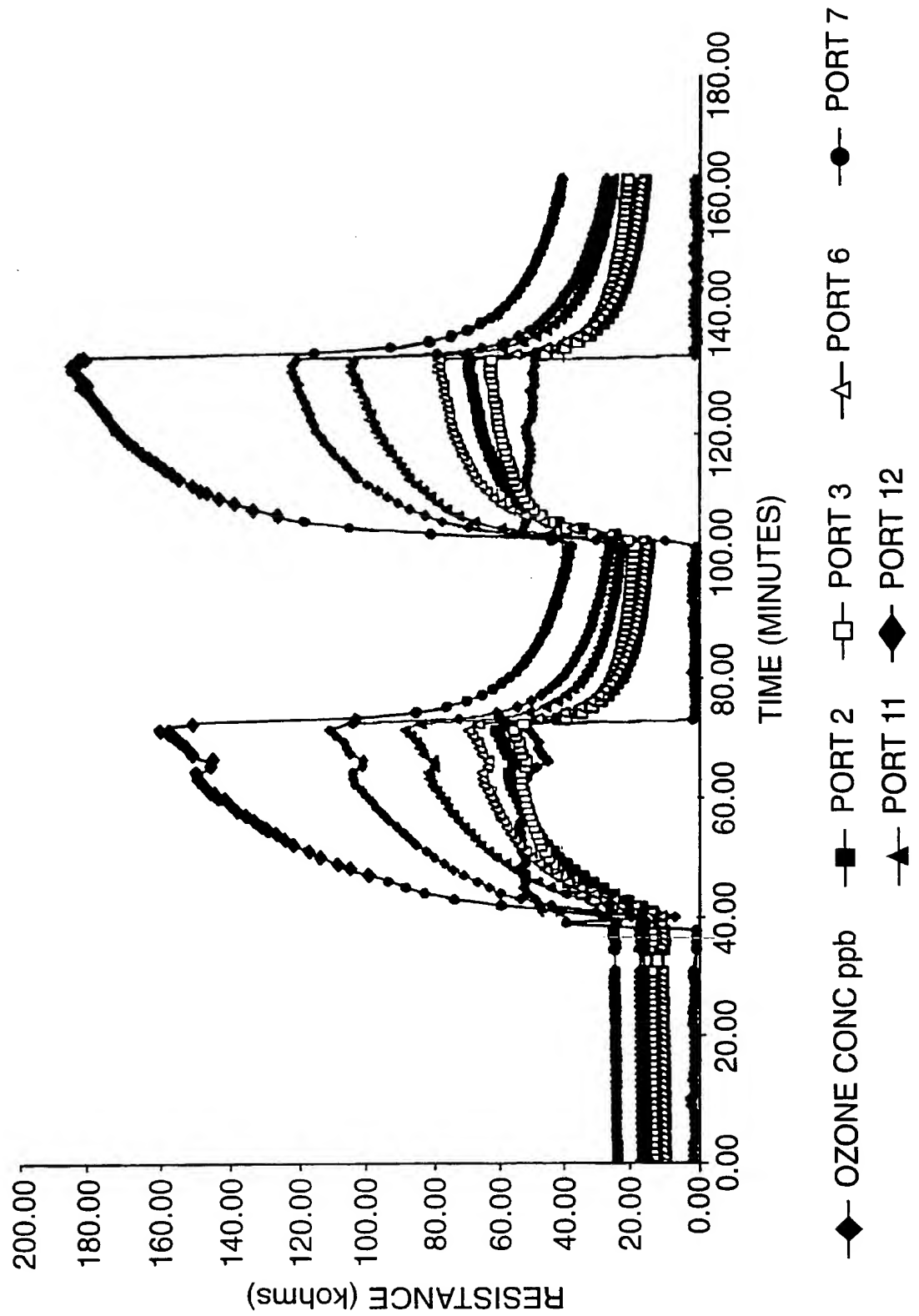
9/10

FIG. 10





10/10

FIG. 11



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P019832WO		FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB99/02757	International filing date (day/month/year) 19/08/1999	Priority date (day/month/year) 03/09/1998	
International Patent Classification (IPC) or national classification and IPC G01N33/00			
Applicant CAPTEUR SENSORS AND ANALYSERS LIMITED et al.			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 15 sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input checked="" type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application 			
Date of submission of the demand 31/03/2000		Date of completion of this report 30.10.2000	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer Diez Schlereth, D Telephone No. +49 89 2399 7488 	

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02757

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

5,6	as originally filed			
1-4,7	as received on	07/09/2000	with letter of	06/09/2000

Claims, No.:

1-6	as received on	07/09/2000	with letter of	06/09/2000
-----	----------------	------------	----------------	------------

Drawings, sheets:

1/9-9/9	as received on	07/09/2000	with letter of	06/09/2000
---------	----------------	------------	----------------	------------

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/02757

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims 1-6
	No: Claims
Inventive step (IS)	Yes: Claims 1-6
	No: Claims
Industrial applicability (IA)	Yes: Claims 1-6
	No: Claims

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

item V.

1.) Reference is made to the following documents:

D1: A. Heilig et al. (1997) Sensors & Actuators B 43, 45-51

D2: WO-A-95/35495

2.) D1, which is considered to be the closest prior art, discloses a method for the quantitative analysis of a mixture of CO and NO₂ in air by sinusoidal modulation of the operating temperature of SnO₂-based thick film gas sensors (see pages 45-46 and Figures 3-6). This document anticipates the subject-matter of claims 1-2, 5 and 8-10.

The subject-matter of claim 1 differs therefrom in that the method comprises (i) increasing the sensor operating temperature to a first temperature to allow the sensor surface to reset then decreasing the sensor operating temperature to a second temperature, and (ii) analysing the resultant resistance of the sensor at the second temperature.

D2 discloses a method for measuring ozone concentration which is based on the use of a resistive gas sensor having a WO₃ sensing element (see Abstract; p. 1, l. 3-8; p. 3, l. 3-26; p. 4, l. 1-19; p. 5, l. 11-22).

In the light of the closest prior art (D1), the technical problem to be solved by the present application was to provide an alternative method of sensing the concentration of an oxidizing gas in a gas mixture.

The solution proposed in claim 1 (and 2-6 as dependent thereon) can be considered novel and inventive within the sense of Art. 33 (2) and (3) PCT for the following reasons:

The resistivity of the sensor in the method of D1 is continuously measured while increasing/decreasing the operating temperature, such as to get a cyclic scan which reflects resistivity values as a function of temperature (see e.g. Figs. 5 & 6). The resistivity of the sensor in the method of D2 is measured while holding the operating temperature at a high constant value.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/02757

The method of claim 1 provides the following advantages over the methods known from the prior art: (i) it results in a significant increase in the stability of the signals generated by the sensor, and (ii) it reduces significantly the lower detection limit of the sensors for ozone.

The skilled person confronted with the above mentioned technical problem and equipped with the teaching of D1-D2 would have had neither motivation nor technical guidance for modifying the method of D1 by measuring resistivity values only at the lower temperature following the temperature pattern "increase/reset/decrease" arriving at a method according to claim 1.

item VII.

Contrary to the requirements of Rule 5.1 (a) (ii) PCT, the relevant background art disclosed in document D1 is not mentioned in the description, nor is this document identified therein.

SEMICONDUCTOR GAS SENSING

This invention relates to the semiconductor gas sensing of oxidising gases such as nitrous and nitric oxide, chlorine, and ozone.

In the following description the invention will be exemplified with reference to ozone sensing, but the general principles are applicable to other oxidising gases. Parts per billion (ppb) quoted hereinafter are by volume.

In our previous application WO-95/35495, we described a method of measurement of ozone concentration involving the measurement of electrical resistance of a porous tungstic oxide element, held at elevated temperature (200-500°C). When the element is held at constant temperature, the sensitivity to ozone tends to vary with time and to be dependent upon the history of the device, including previous exposure to ozone. Other semiconducting oxides have been shown to exhibit resistance increases at elevated temperature in the presence of small concentrations of ozone in the air: In_2O_3 , pure and variously doped, by Takada et al, Sensors & Actuators B : Chemical 13 (1993) 404; MoO_3 by Garlo et al., Sensors & Actuators B : Chemical 47 (1998) 92. We have now discovered that SnO_2 also shows the effect (see Figure 1), though at rather lower temperature (~200°C) and with problems of baseline stability. We believe that the phenomenon is generic to a certain general class of semiconducting oxides for which oxygen vacancies can be created at the surface, at the operating temperature, in air, in sufficient concentration to substantially affect the concentration of electronic charge carriers and hence the electrical conductivity.

The invention is defined by the claims hereinafter.

We have discovered a method for analysis of ozone concentration in air, which is generally applicable to the afore-mentioned class of oxides.

The method surprisingly results in (1) a significant increase in the stability of the signals generated by sensors incorporating these materials, and (2) significantly reduces the lower detection limit of the sensors for ozone to concentrations of a

AMENDED SHEET

few ppb, which is typical of the UV ozone analysers conventionally employed to detect this molecule. The method involves causing a perturbation of the temperature of the sensor and analysing the resulting time variation of the sensor resistance or conductance.

The method gives substantially increased accuracy and stability, and consequently a greater reliability of measurement, especially at very low ozone concentration (less than 100 ppb in air). A very low detection limit for ozone can be achieved, which can be reliably sustained in measurement over a long period of time. A typical detection limit achieved using a device based on WO_3 is 2.5 ppb in air, reliably sustained without change of calibration over at least 3 months.

Preferred features of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a graph showing the response of an SnO_2 sensor operated at 175°C to a pulse of 50 ppb ozone in air,

Figure 2 is a graph showing the response of a WO_3 sensor to 50 ppb ozone in air after having been stepped to 600°C from an operating temperature of 400°C ,

Figures 3 and 4 show the variations in time constants of equation (1) hereinafter with ozone concentration,

Figure 5 shows the variation in resistance of the WO_3 sensor to ozone concentration and the result of curve fitting applied thereto,

AMENDED SHEET

Figure 6 shows the response of the WO_3 sensor to ozone concentration over a period of days,

Figure 7 is a graph illustrating the time required to reset the sensor surface as a function of reset temperature,

Figure 8 is a graph illustrating the energy consumed in resetting the sensor surface, as a function of reset temperature,

Figure 9 compares the results of employing a WO_3 sensor according to the invention to monitor street level ozone concentration as compared to similar results obtained with a conventional UV absorption instrument, and

Figure 10 compares the results of employing a WO_3 sensor according to the invention to provide a vertical profile of ozone in the atmosphere as compared to similar results obtained with a conventional instrument,

The invention involves perturbing the sensor as follows:

- step to a high temperature to reset the surface
- step back to a low temperature to make the measurement
- analyse the variation of resistance with time at the low temperature to obtain the ozone concentration
- repeat the sequence.

For example with a device based on WO_3 , the "high" temperature can be 400°C - 800°C and the "low" temperature can be 200°C - 500°C , with the obvious constraint that the "high" temperature should be greater than the "low" temperature.

Figure 2 shows an example of this. In the presence of ozone in the air,

AMENDED SHEET

the device temperature was stepped to 600°C for 300s, then stepped back to 400°C for 300s. The time-variation of resistance at 400°C following the step back ($t=0$) is shown. The conductivity, S (reciprocal of resistance) at the low temperature shows the following variation:

$$S(t) = S_{lim} + a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (1)$$

where

$$S_{lim} = S_{\infty} + b_2/(O_3)$$

$$\tau_1 = b_1/(O_3)$$

$$\tau_2 = b_2/(O_3)$$

where (O_3) denotes the ozone concentration.

Here, S_{∞} , a_1 are constants which depend on the time and temperature of the "high" temperature step. The b_i depend upon the temperature of the "low" temperature step, at which the measurement is made but do not depend on the high temperature step values. Typically, $b_2 \approx 10b_1$, so that the second time-dependent term is only significant at higher ozone concentration. If the measurement temperature (the "low" temperature) is decreased then the ratio b_2/b_1 increases, so again the second time-dependent term becomes less significant.

Application of method to ozone measurement

(a) by curve-fitting the data to equation (1), the values of τ_1 , τ_2 are determined. By reference to a calibration curve of τ_1 (and if necessary τ_2) against ozone concentration, the ozone concentration is obtained. The sensor and the stability of the operating circuitry are checked by checking the stability of the parameters S_{∞} , a_1 , a_2 , which are also obtained from the fit. If the measurement time is limited, or the ozone concentration is low enough, or the measurement temperature is low enough, then only one time constant will be required to describe the data, and the reliability of the parameter fit can be improved.

In the example shown in Figure 2, the fitted curve provided the values τ_1

well as with a conventional UV absorption instrument. The two types of measurements agree generally quite well.

Figure 10 shows the results of vertical profiling for ozone in the atmosphere using a WO_3 sensor given a single high temperature reset pulse, and the equivalent results from a conventional ECC ozone sonde. Again, the results agree generally well.

AMENDED SHEET

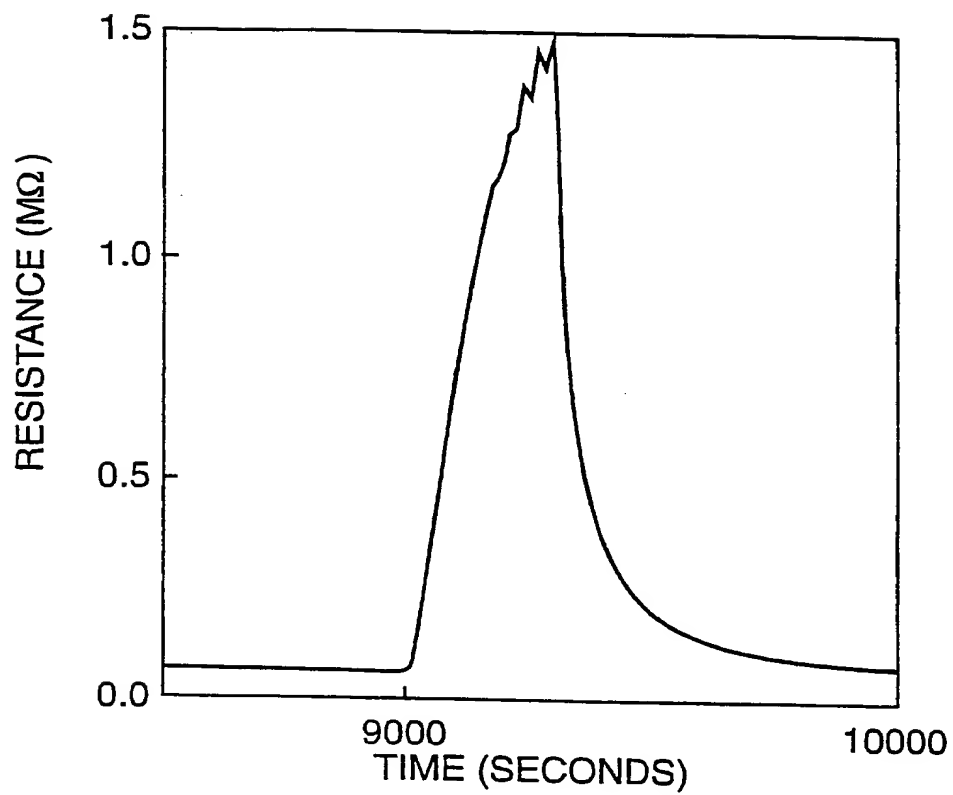
Claims:-

1. A method of sensing the concentration of an oxidising gas in a gas mixture using a semiconductor gas sensor having a resistivity sensitive to the oxidising gas, which comprises increasing the sensor operating temperature to a first
5 temperature to allow the sensor surface to reset then decreasing the sensor operating temperature to a second temperature and analysing the resultant resistance of the sensor at the second temperature.
2. A method according to claim 1 in which the first temperature is 400 to 800°C and the second temperature is 200 to 500°C.
- 10 3. A method according to claim 1 or 2 wherein the sensor resistance is analyzed as a function of time.
4. A method according to any preceding claim in which the oxidising gas is NO₂, NO, Cl₂, or O₃.
5. A method according to any preceding claim in which the sensor is a layer of
15 WO₃, In₂O₃, MoO₃ or SnO₂.
6. A method according to claim 5 wherein the sensor is a layer of WO₃ and the oxidising gas is O₃.

AMENDED SHEET

1/9

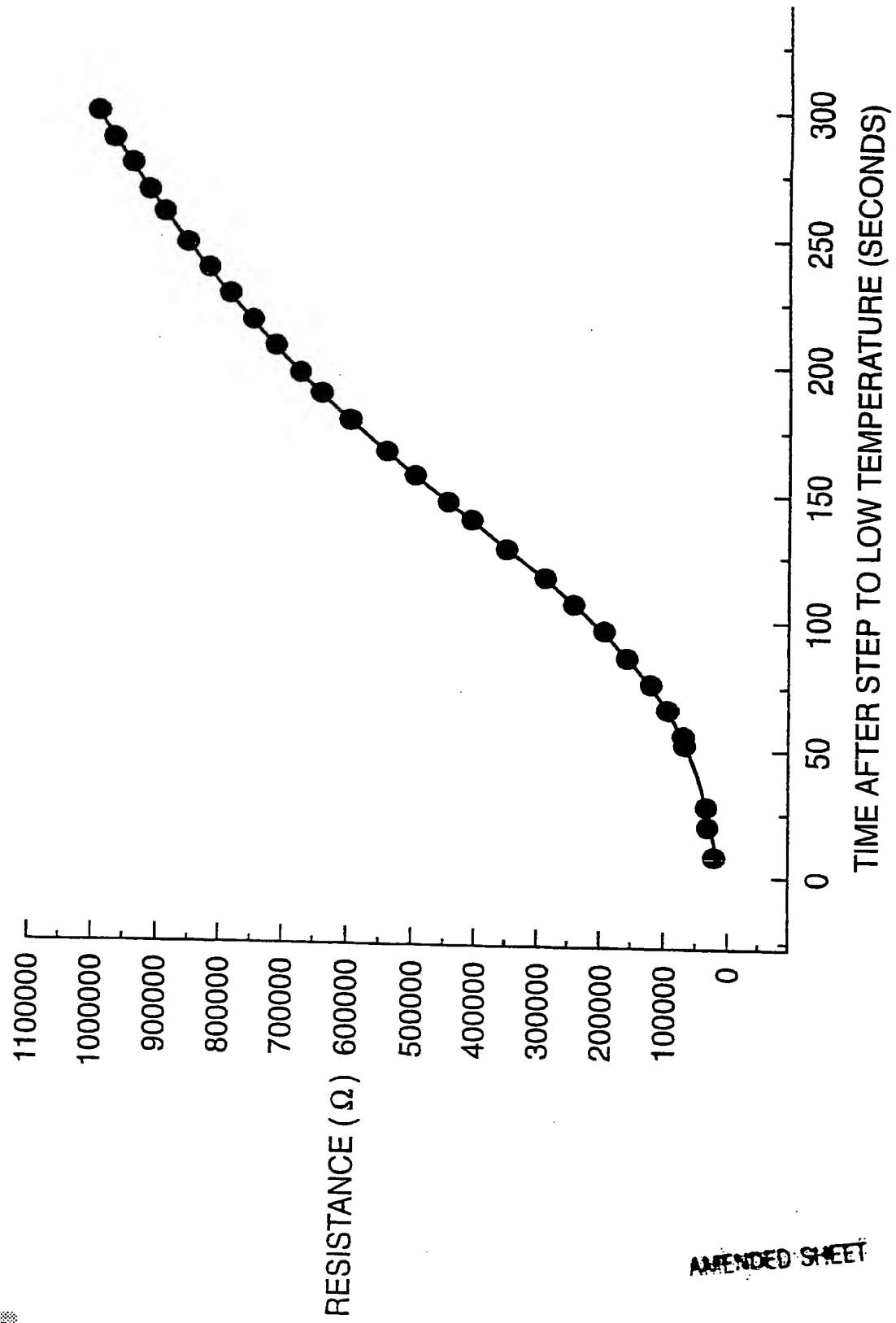
FIG. 1



AMENDED SHEET

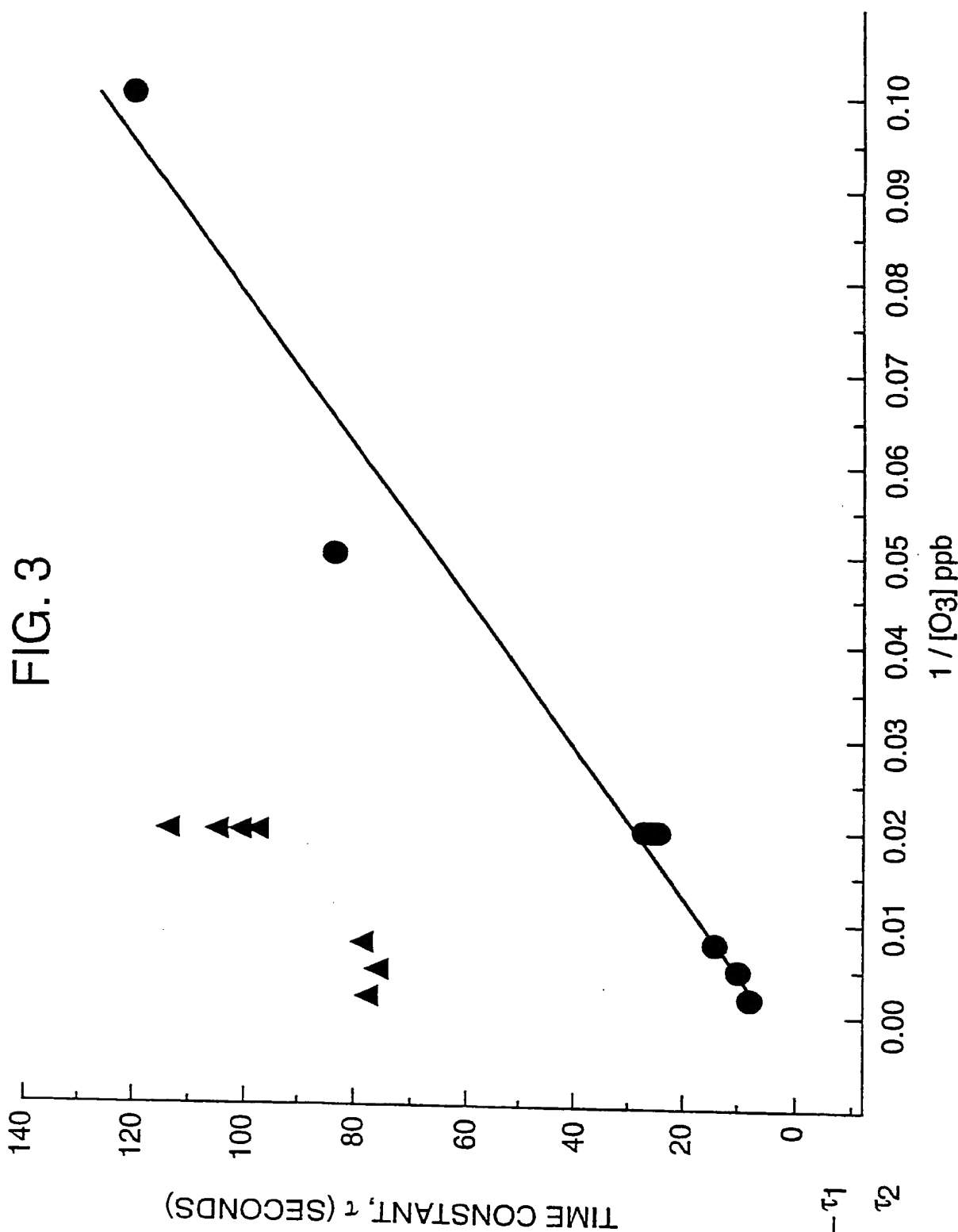
2/9

FIG. 2



APPENDED SHEET

3/9



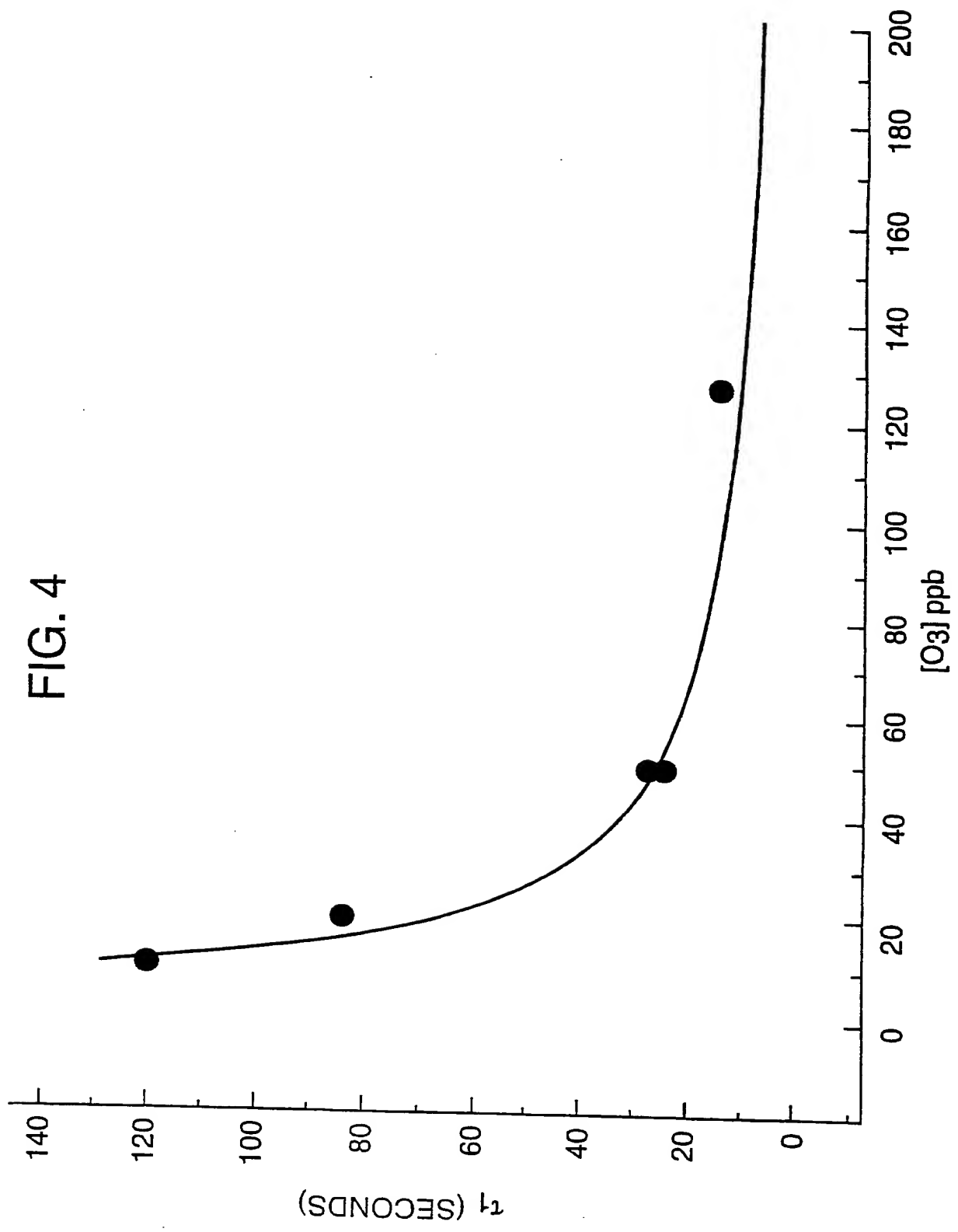
AMENDED SHEET

τ_1

τ_2

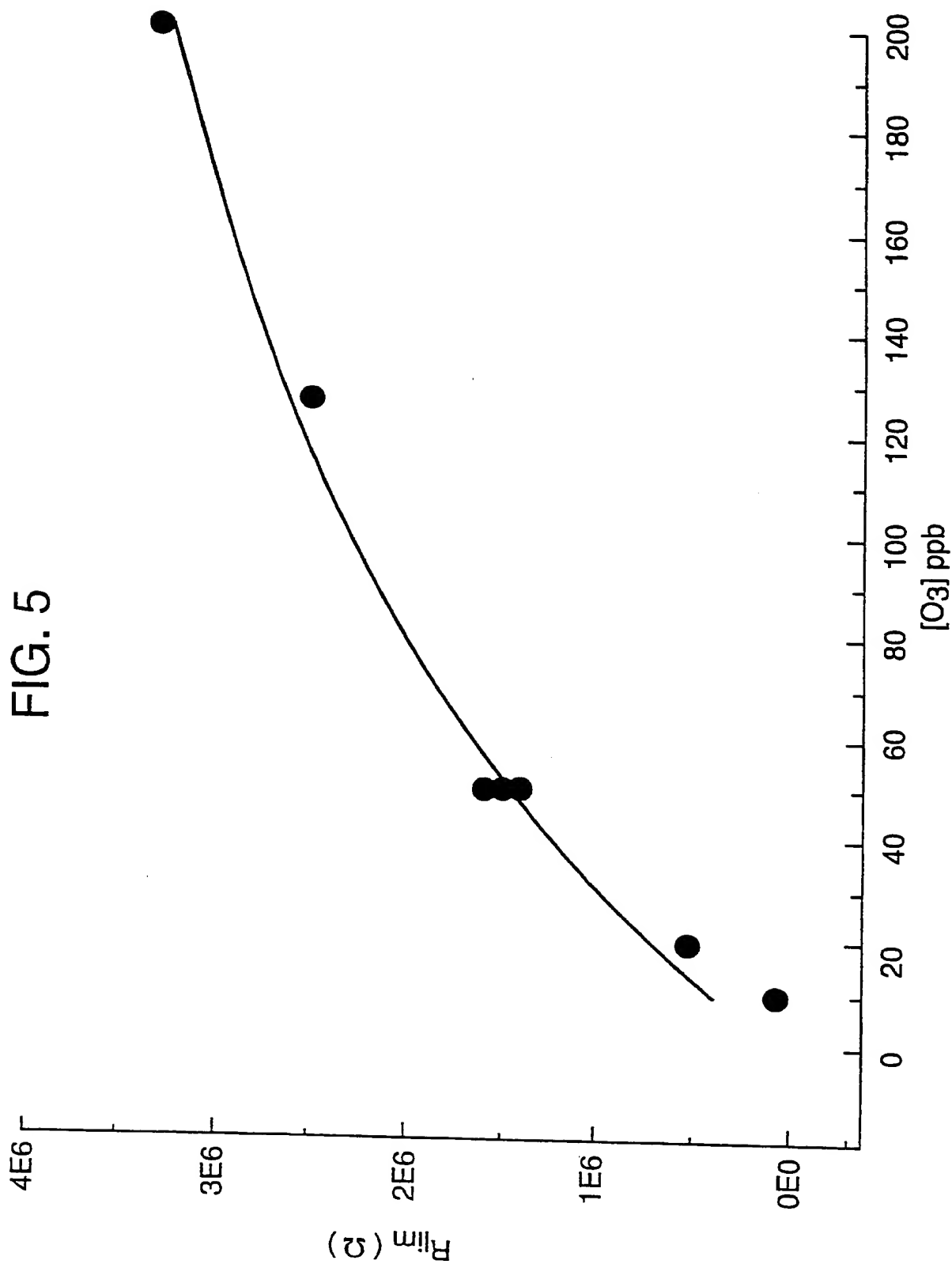
4/9

FIG. 4



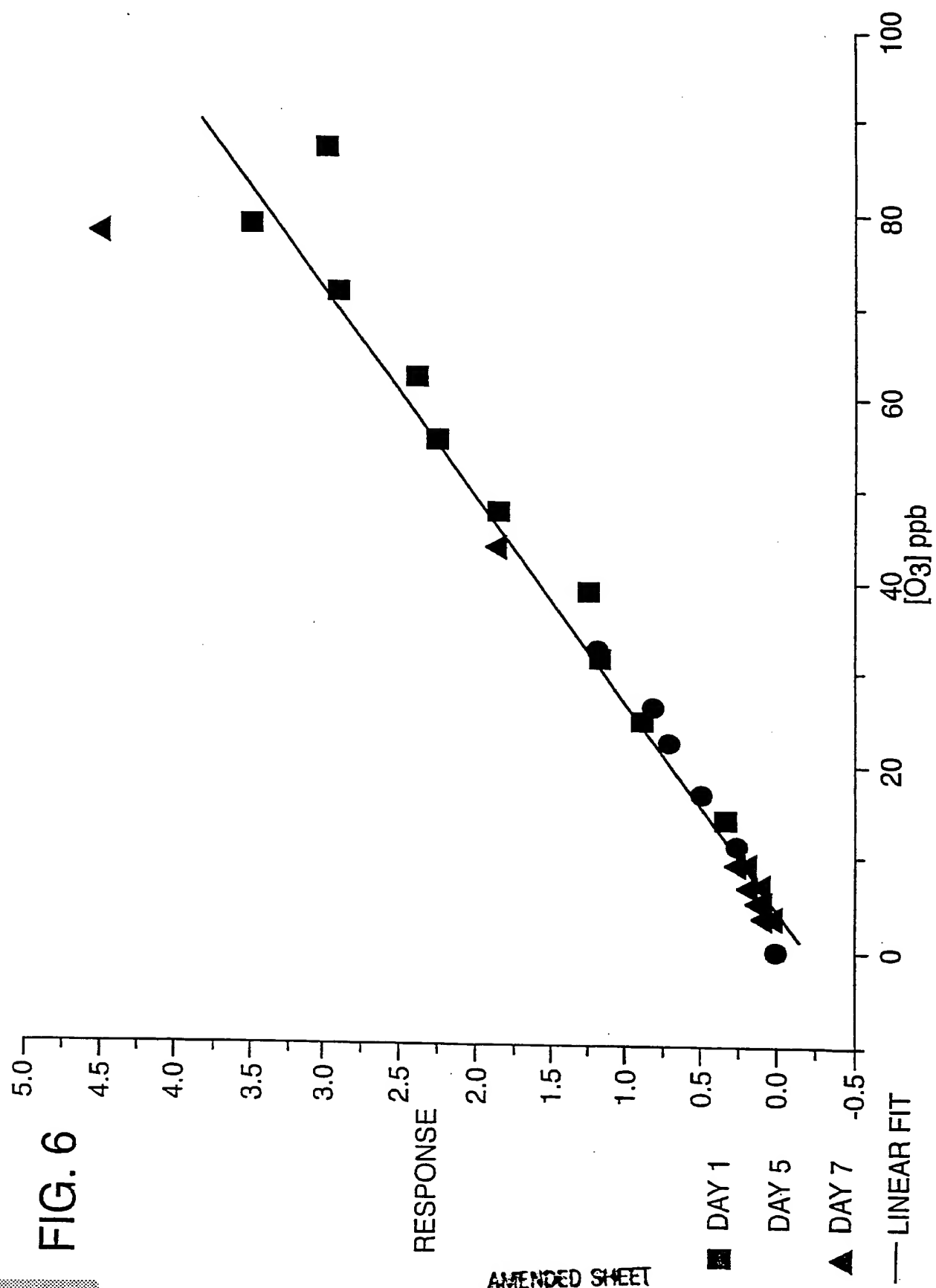
AMENDED SHEET

5/9



AMENDED SHEET

6/9



7/9

FIG. 7

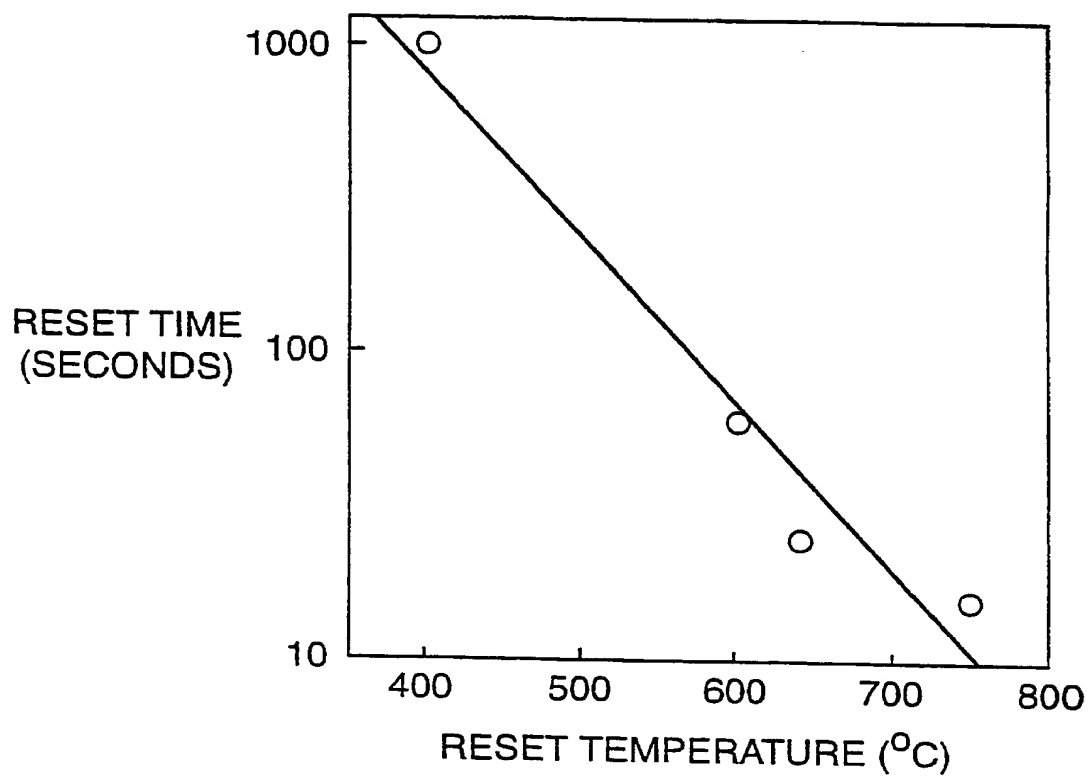


FIG. 8

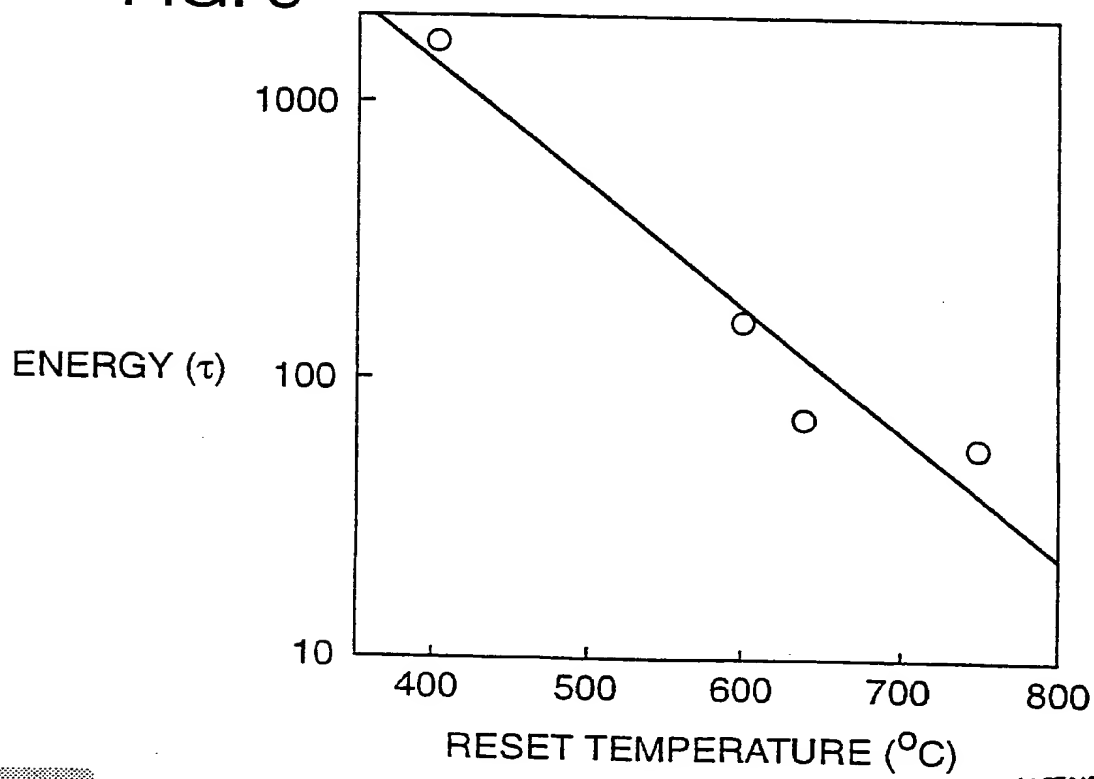
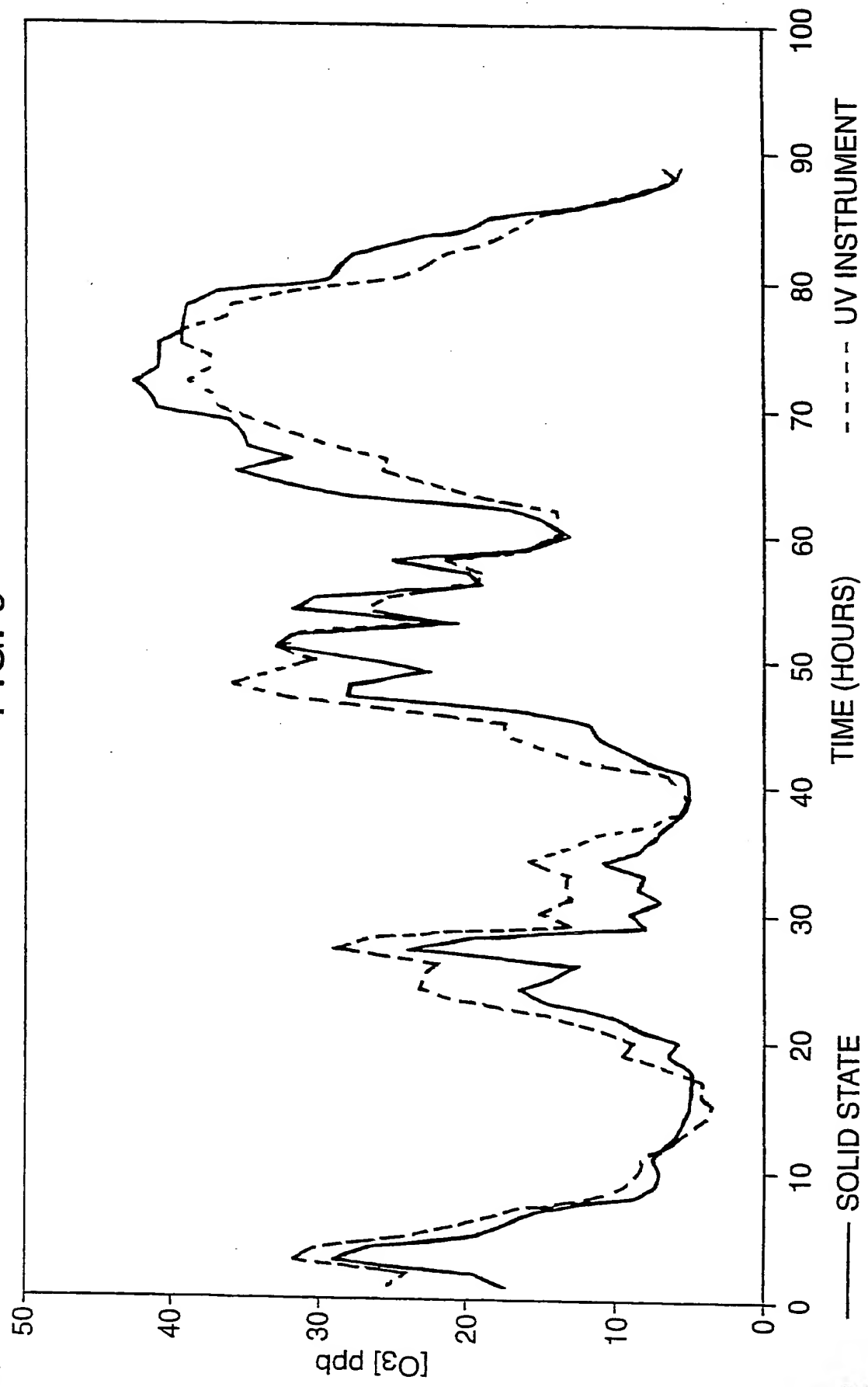
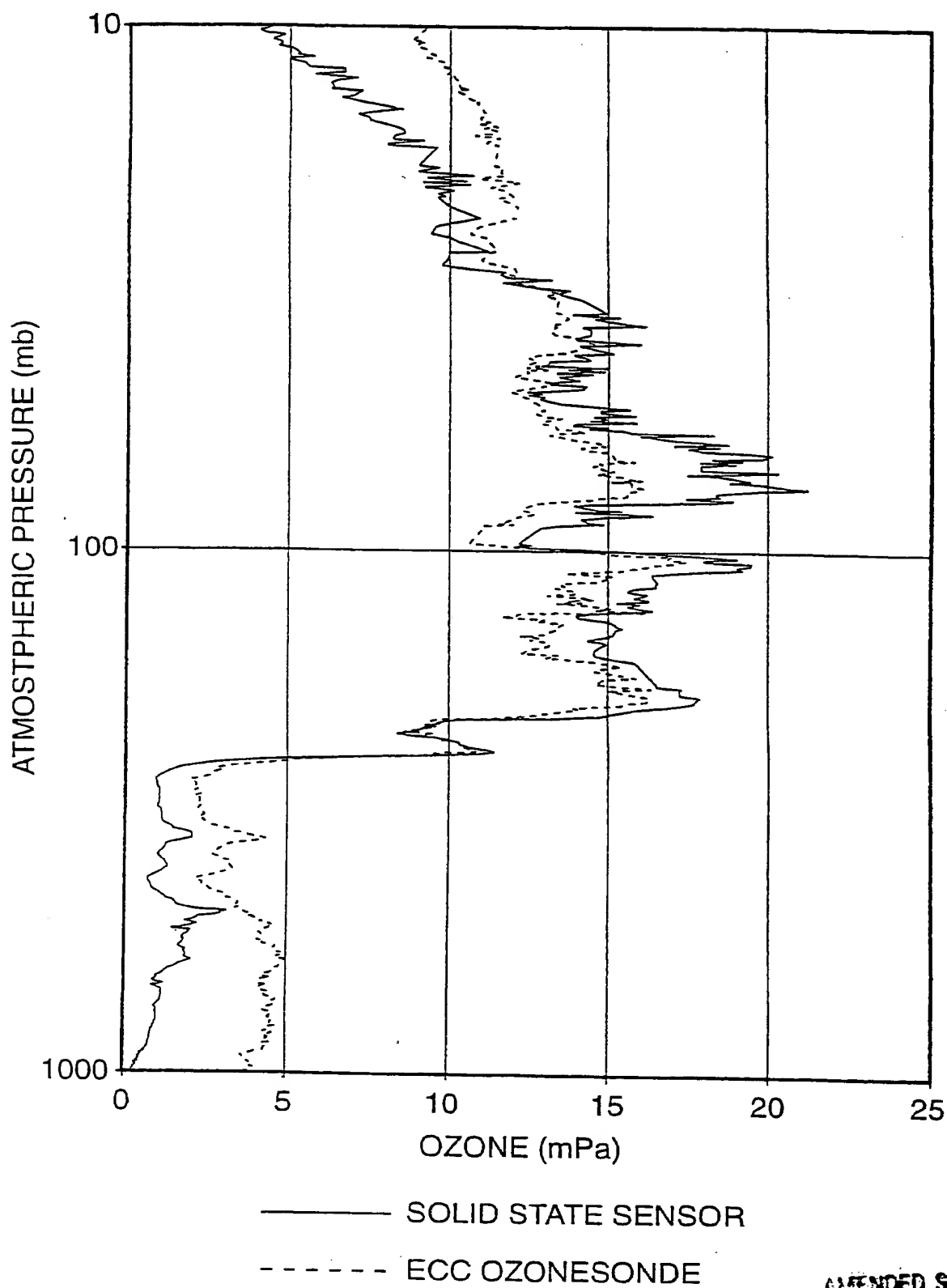


FIG. 9



9/9

FIG. 10



ATTENDED SHEET

MAR 2001

CLAIMS:-

1. A method of sensing the concentration of an oxidising gas in a gas mixture using a semiconductor gas sensor having a resistivity sensitive to the oxidising gas, which comprises perturbing the sensor operating temperature and
5 analysing the resultant resistance of the sensor following perturbation.
2. A method according to claim 1, in which the perturbation is a square wave pulse or is sinusoidal.
3. A method according to claim 1 or 2 in which the perturbation comprises increasing the sensor temperature followed by a temperature reduction at which
10 the resistance is analysed.
4. A method according to claim 3 wherein the increased sensor temperature is 400 to 800°C and the reduced temperature is 200 to 500°C.
5. A method according to any preceding claim wherein the sensor resistance is analysed as a function of time.
- 15 6. A method of sensing the concentration of an oxidising gas in a gas mixture using a semiconducting gas sensor having a resistivity sensitive to the oxidising gas, which comprises perturbing the oxidising gas concentration over the sensor and analysing the resultant resistance of the sensor following perturbation.
7. A method according to claim 6 wherein the perturbation comprises reducing
20 the oxidising gas concentration to zero or periodically changing the flow rate of gas over the sensor.
8. A method according to any preceding claim in which the sensor is a semiconductor oxide for which oxygen vacancies can be created at the sensor surface, at the operating temperature, in air, in sufficient concentration to affect
25 substantially the concentration of electronic charge carriers and hence the resistivity.
9. A method according to claim 8 in which the sensor is WO_3 , In_2O_3 , MoO_3 or SnO_2 .
10. A method according to any preceding claim in which the oxidising gas is

NO₂, NO, Cl₂, or O₃.

11. A method according to claim 10 wherein the gas is O₃ and the sensor is WO₃.

12. An apparatus for conducting the method of any of claims 1 to 11.

well as with a conventional UV absorption instrument. The two types of measurements agree generally quite well.

Figure 10 shows the results of vertical profiling for ozone in the atmosphere using a WO_3 sensor given a single high temperature reset pulse, and the equivalent results from a conventional ECC ozone sonde. Again, the results agree generally well.

Method 2

- oscillate the temperature by a relatively small amount e.g. $\pm 50^\circ\text{C}$
- either a square-wave oscillation between two temperatures separated by a small amount (e.g. 50°C), with a period of typically 1-10 min, or a sinusoidal oscillation with a period of typically 1-10min
- measure the phase shift (delay time) between temperature oscillation and resistance oscillation and determine ozone concentration from a calibration curve.

In this method, there will, of course, be an oscillation of resistance caused by the effect of temperature on the resistivity of the material (resistance decreases with increasing temperature). This element of the oscillating resistance will have only a small delay time (typically $\sim 0.2\text{s}$) determined by the thermal response time of the sensor. Superimposed upon this will be an additional oscillation due to the effect of ozone. The two effects can be separated using a time-gated measurement scheme. Alternatively, the device can be configured as a multi-electrode device of the type we have previously described in EP-B-591240. If such a device having two electrode spacings is arranged in a bridge circuit, then the output signal will be proportional to the ratio of the two resistances. This resistance ratio will be independent of temperature in the absence of ozone, but, because ozone is a reactive gas which shows a concentration gradient through the sensor layer, the resistance ratio will vary if ozone is present, dependent upon both time and temperature.

SEMICONDUCTOR GAS SENSING

This invention relates to the semiconductor gas sensing of oxidising gases such as nitrous and nitric oxide, chlorine, and ozone.

In the following description the invention will be exemplified with reference to ozone sensing, but the general principles are applicable to other oxidising gases. Parts per billion (ppb) quoted hereinafter are by volume.

In our previous application WO-95/35495, we described a method of measurement of ozone concentration involving the measurement of electrical resistance of a porous tungstic oxide element, held at elevated temperature (200-500°C). When the element is held at constant temperature, the sensitivity to ozone tends to vary with time and to be dependent upon the history of the device, including previous exposure to ozone. Other semiconducting oxides have been shown to exhibit resistance increases at elevated temperature in the presence of small concentrations of ozone in the air: In_2O_3 , pure and variously doped, by Takada et al, Sensors & Actuators B : Chemical 13 (1993) 404; MoO_3 by Garlo et al., Sensors & Actuators B : Chemical 47 (1998) 92. We have now discovered that SnO_2 also shows the effect (see Figure 1), though at rather lower temperature (~200°C) and with problems of baseline stability. We believe that the phenomenon is generic to a certain general class of semiconducting oxides for which oxygen vacancies can be created at the surface, at the operating temperature, in air, in sufficient concentration to substantially affect the concentration of electronic charge carriers and hence the electrical conductivity.

The invention is defined by the claims hereinafter.

We have discovered a set of methods for analysis of ozone concentration in air, which are generally applicable to the afore-mentioned class of oxides. The methods surprisingly result in (1) a significant increase in the stability of the signals generated by sensors incorporating these materials, and (2) significantly reduce the lower detection limit of the sensors for ozone to concentrations of a

few ppb, which is typical of the UV ozone analysers conventionally employed to detect this molecule. These methods involve causing a perturbation of the condition of the sensor and analysing the resulting time variation of the sensor resistance or conductance. These methods are:

5 (1) a perturbation of the sensor temperature, which may be small or large, in the form of a square pulse or a sinusoidal variation,

(2) a perturbation of the ozone concentration near the sensor, either by periodically switching the gas flow to the sensor through a catalyst bed which destroys any ozone present, or by simply altering the flow rate of gas over the
10 sensor, using the hot sensor itself to cause local decomposition of the ozone present in the air.

The methods give substantially increased accuracy and stability, and consequently a greater reliability of measurement, especially at very low ozone concentration (less than 100 ppb in air). A very low detection limit for ozone can
15 be achieved, which can be reliably sustained in measurement over a long period of time. A typical detection limit achieved using a device based on WO_3 is 2.5 ppb in air, reliably sustained without change of calibration over at least 3 months.

Preferred features of the invention will now be described, by way of
20 example, with reference to the accompanying drawings, in which:

Figure 1 is a graph showing the response of an SnO_2 sensor operated at 175°C to a pulse of 50 ppb ozone in air,

Figure 2 is a graph showing the response of a WO_3 sensor to 50 ppb ozone in air after having been stepped to 600°C from an operating temperature
25 of 400°C ,

Figures 3 and 4 show the variations in time constants of equation (1) hereinafter with ozone concentration,

Figure 5 shows the variation in resistance of the WO_3 sensor to ozone concentration and the result of curve fitting applied thereto,

Figure 6 shows the response of the WO_3 sensor to ozone concentration over a period of days,

Figure 7 is a graph illustrating the time required to reset the sensor surface as a function of reset temperature,

5 Figure 8 is a graph illustrating the energy consumed in resetting the sensor surface, as a function of reset temperature,

Figure 9 compares the results of employing a WO_3 sensor according to the invention to monitor street level ozone concentration as compared to similar results obtained with a conventional UV absorption instrument,

10 Figure 10 compares the results of employing a WO_3 sensor according to the invention to provide a vertical profile of ozone in the atmosphere as compared to similar results obtained with a conventional instrument,

Figure 11 shows the response of a number of WO_3 sensors operated according to the invention when subjected to pulses of ozone, and

15 Figure 12 shows the effect of air flow rate on a WO_3 sensor operated according to the invention.

The invention employs different methods to perturb the sensor and to analyse the results, as will now be described.

20 Method 1: - step to a high temperature to reset the surface
 - step back to a low temperature to make the measurement
 - analyse the variation of resistance with time at the low
 temperature to obtain the ozone concentration
 - repeat the sequence.

25 For example with a device based on WO_3 , the "high" temperature can be 400°C - 800°C and the "low" temperature can be 200°C - 500°C , with the obvious constraint that the "high" temperature should be greater than the "low" temperature.

Figure 2 shows an example of this. In the presence of ozone in the air,

the device temperature was stepped to 600°C for 300s, then stepped back to 400°C for 300s. The time-variation of resistance at 400°C following the step back ($t=0$) is shown. The conductivity, S (reciprocal of resistance) at the low temperature shows the following variation:

$$S(t) = S_{lim} + a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (1)$$

where

$$S_{lim} = S_{\infty} + b_0/(O_3)$$

$$\tau_1 = b_1/(O_3)$$

$$\tau_2 = b_2/(O_3)$$

where (O_3) denotes the ozone concentration.

Here, S_{∞} , a_i are constants which depend on the time and temperature of the "high" temperature step. The b_i depend upon the temperature of the "low" temperature step, at which the measurement is made but do not depend on the high temperature step values. Typically, $b_2 \approx 10b_1$, so that the second time-dependent term is only significant at higher ozone concentration. If the measurement temperature (the "low" temperature) is decreased then the ratio b_2/b_1 increases, so again the second time-dependent term becomes less significant.

Application of method to ozone measurement

(a) by curve-fitting the data to equation (1), the values of τ_1 , τ_2 are determined. By reference to a calibration curve of τ_1 (and if necessary τ_2) against ozone concentration, the ozone concentration is obtained. The sensor and the stability of the operating circuitry are checked by checking the stability of the parameters S_{∞} , a_1 , a_2 , which are also obtained from the fit. If the measurement time is limited, or the ozone concentration is low enough, or the measurement temperature is low enough, then only one time constant will be required to describe the data, and the reliability of the parameter fit can be improved.

In the example shown in Figure 2, the fitted curve provided the values τ_1

1/10

FIG. 1

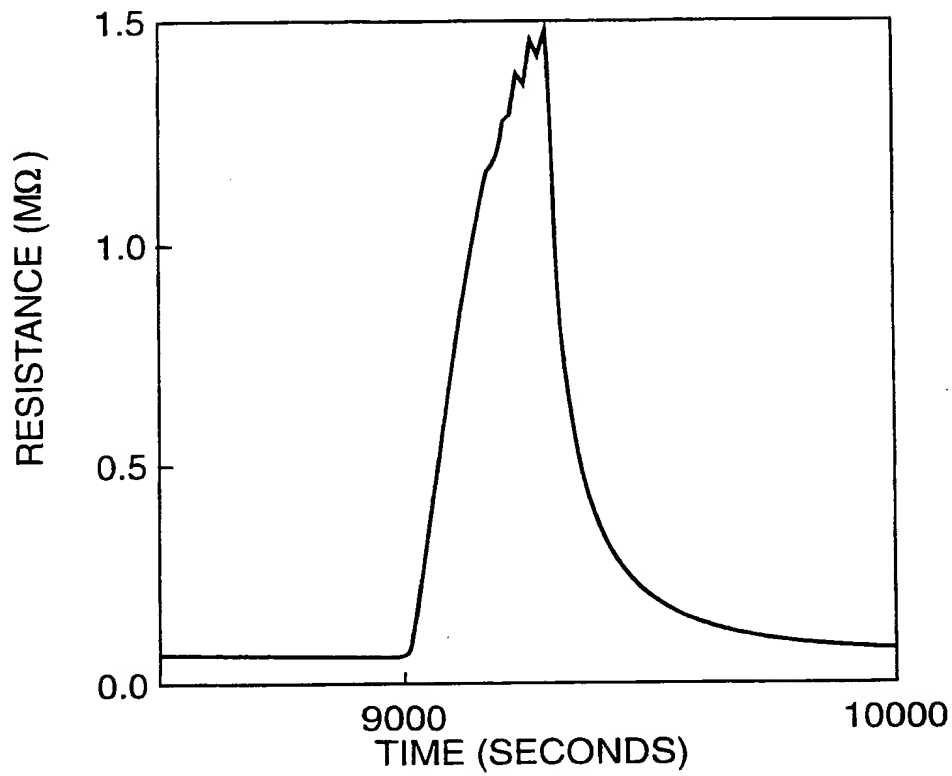
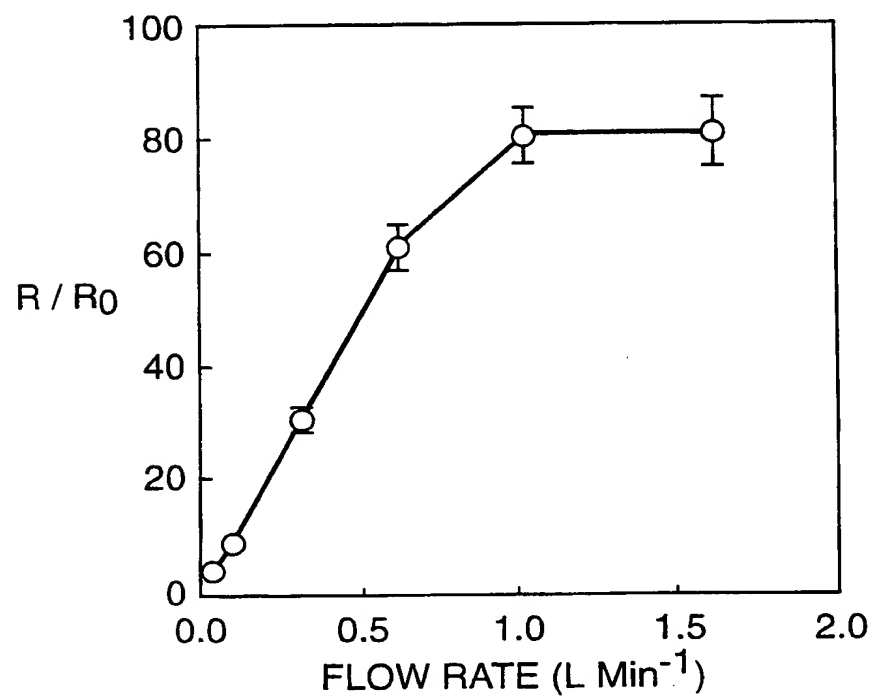
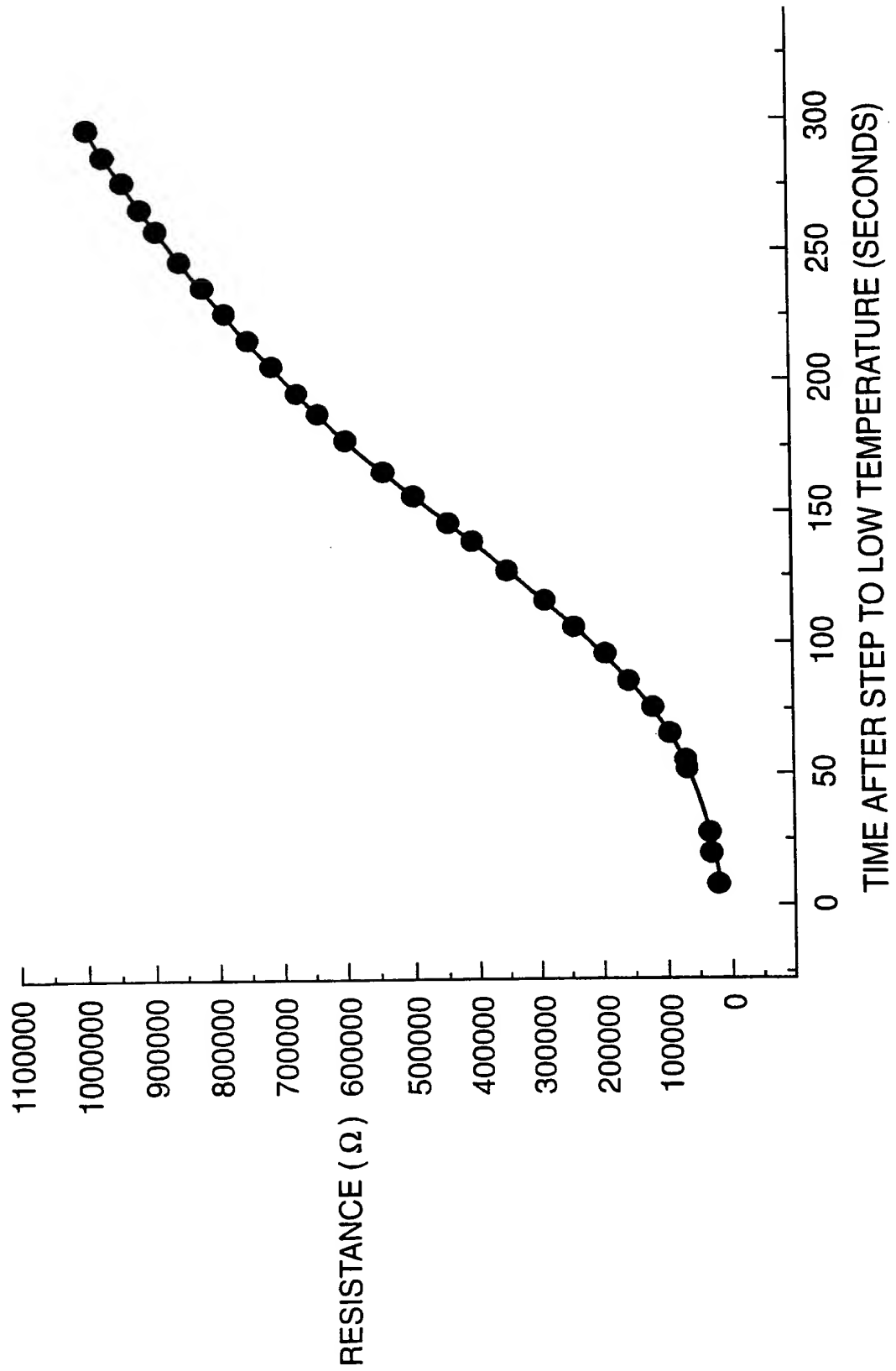


FIG. 12

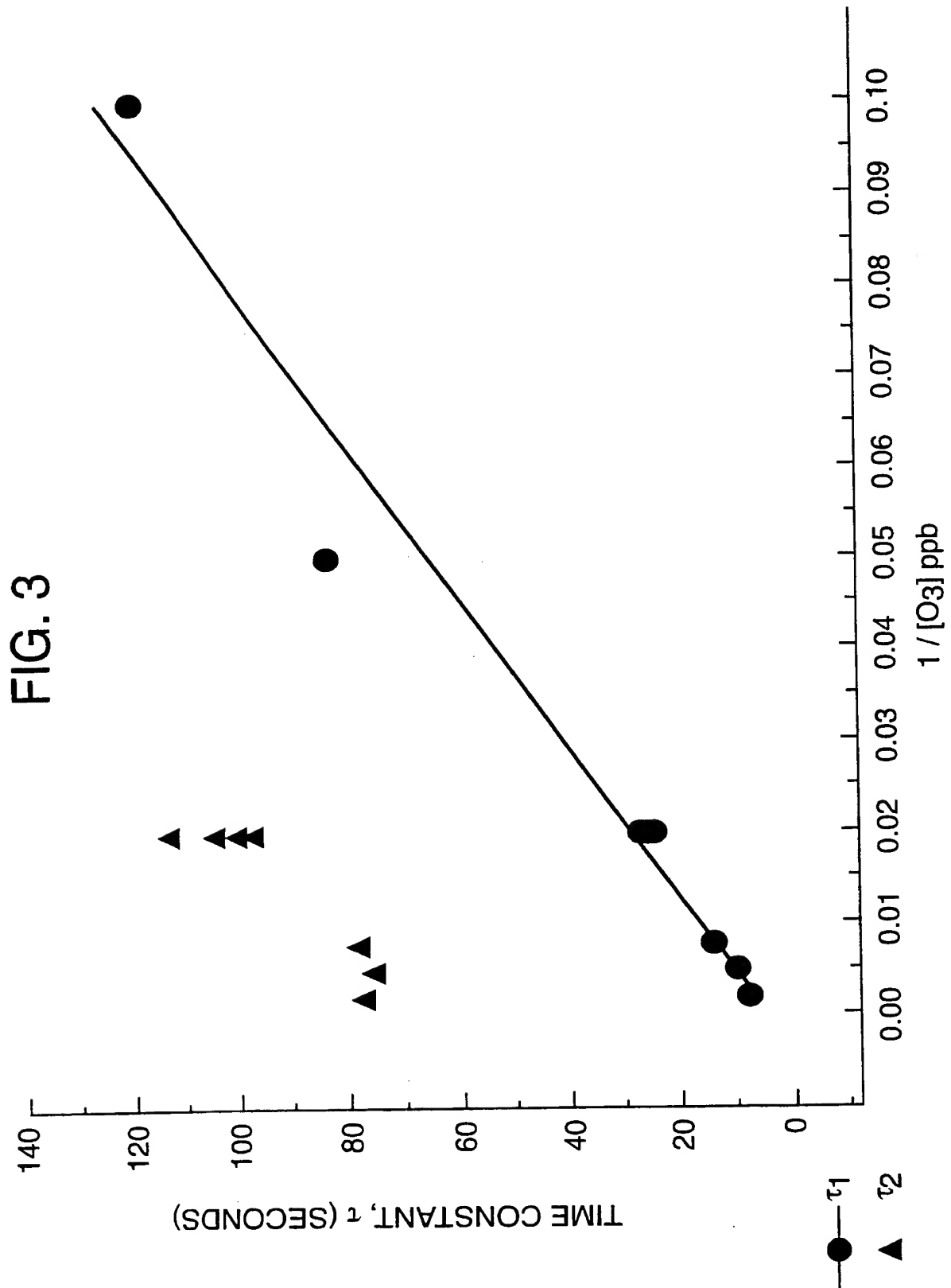


2/10

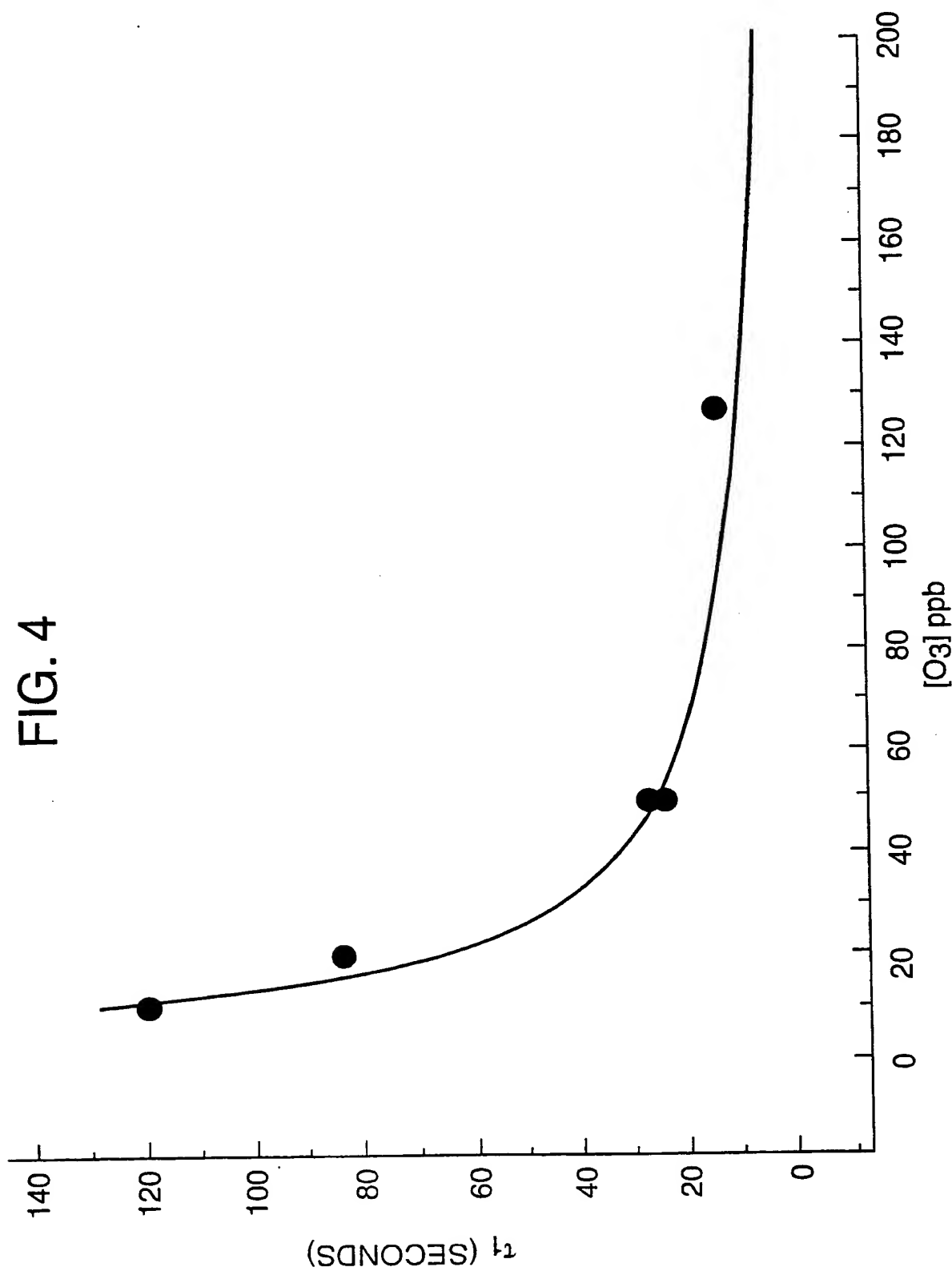
FIG. 2



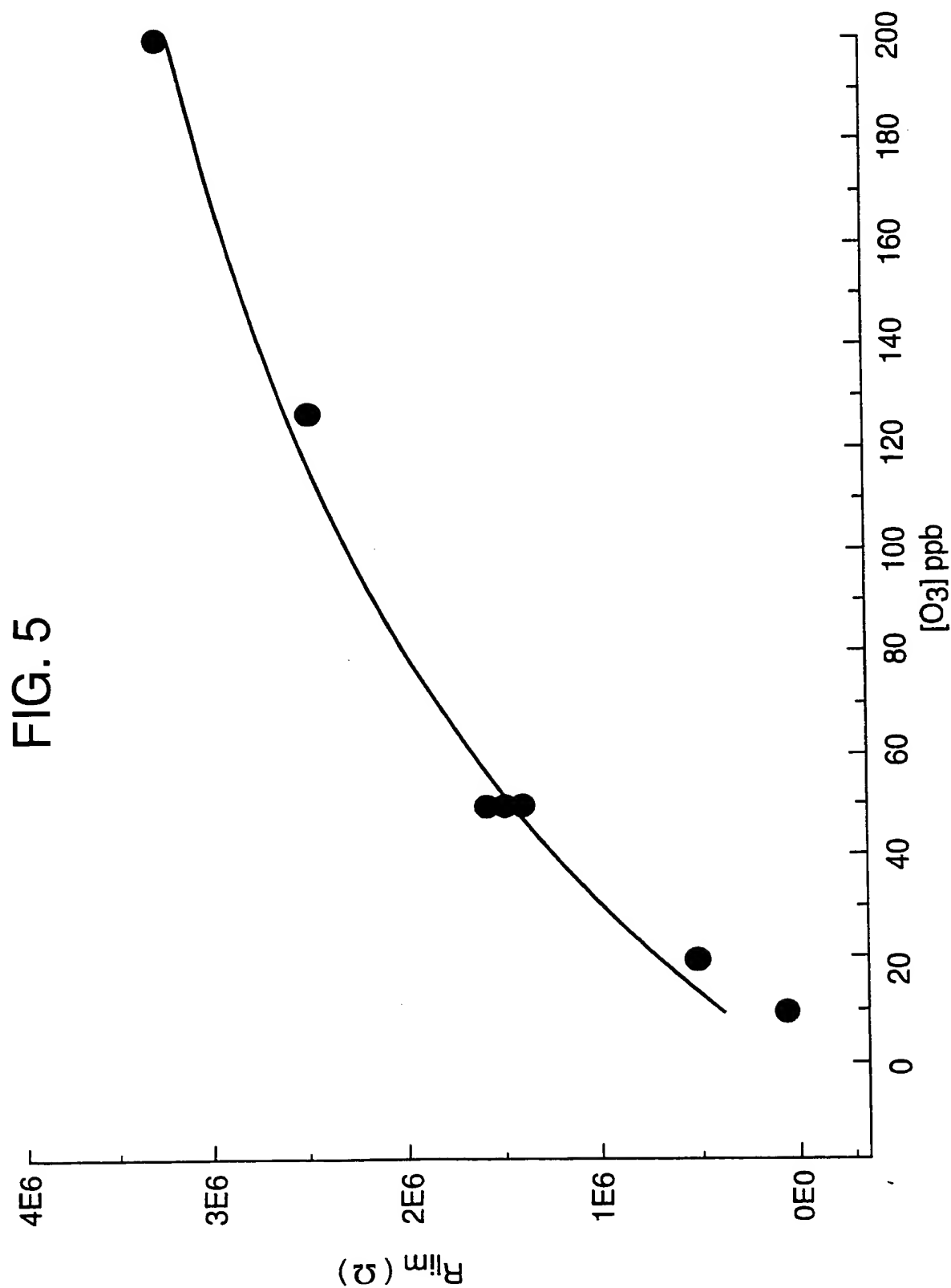
3/10



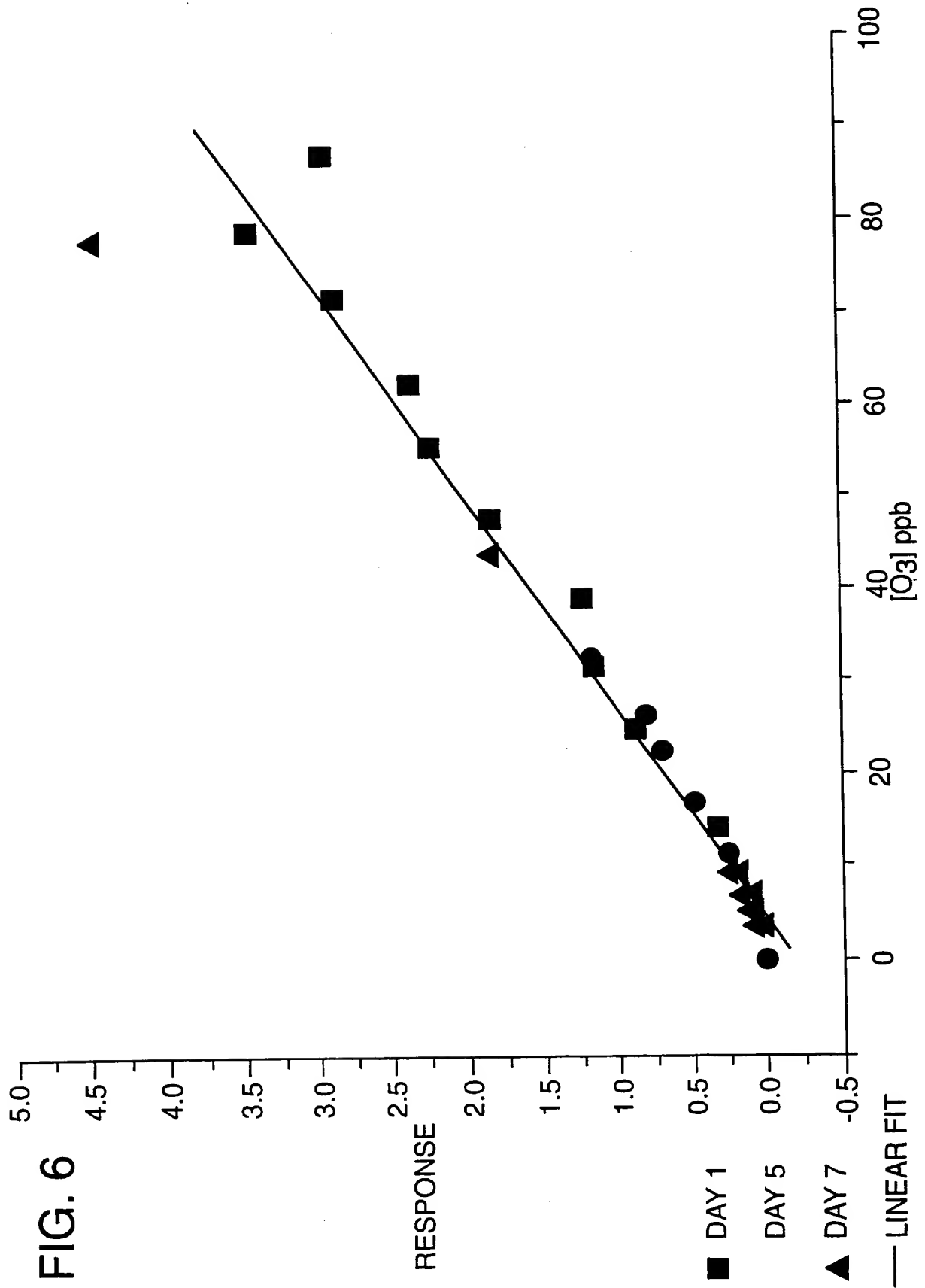
4/10



5/10



6/10



7/10

FIG. 7

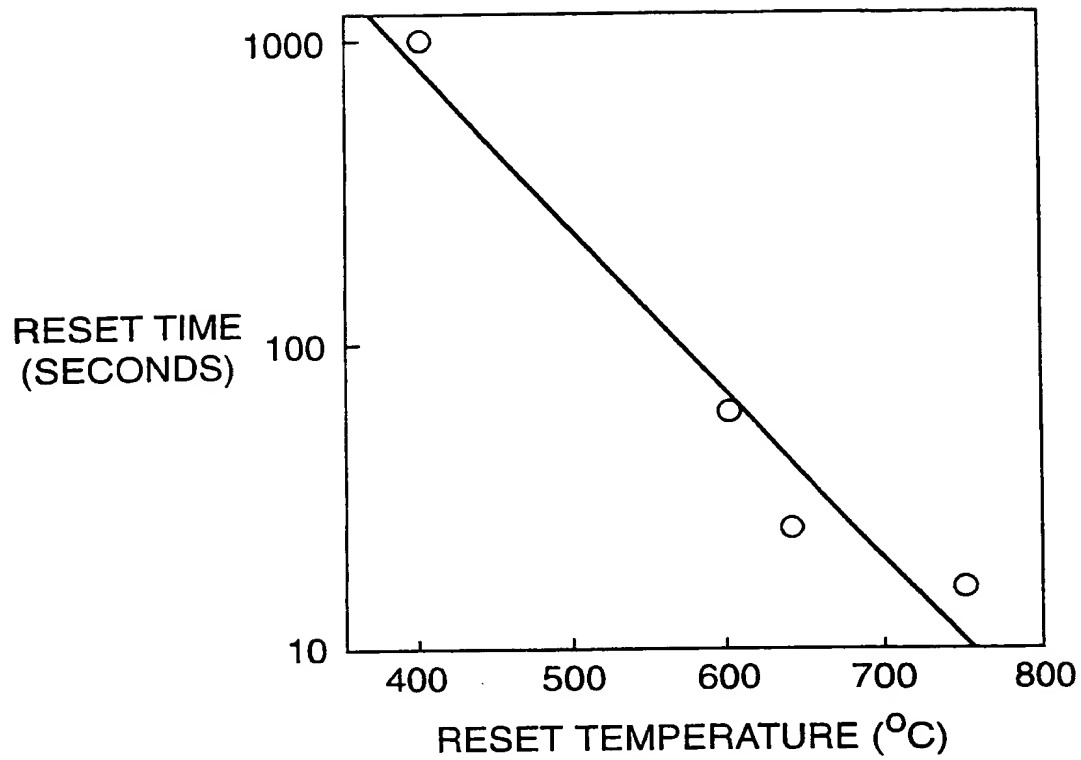


FIG. 8

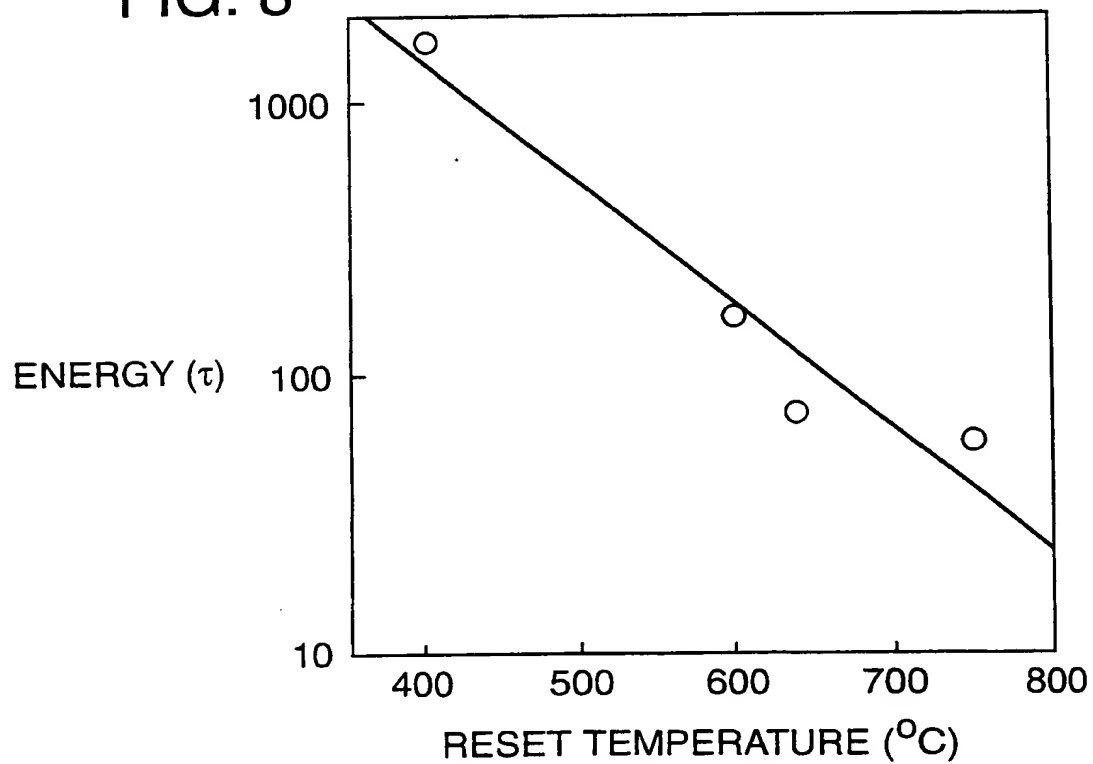
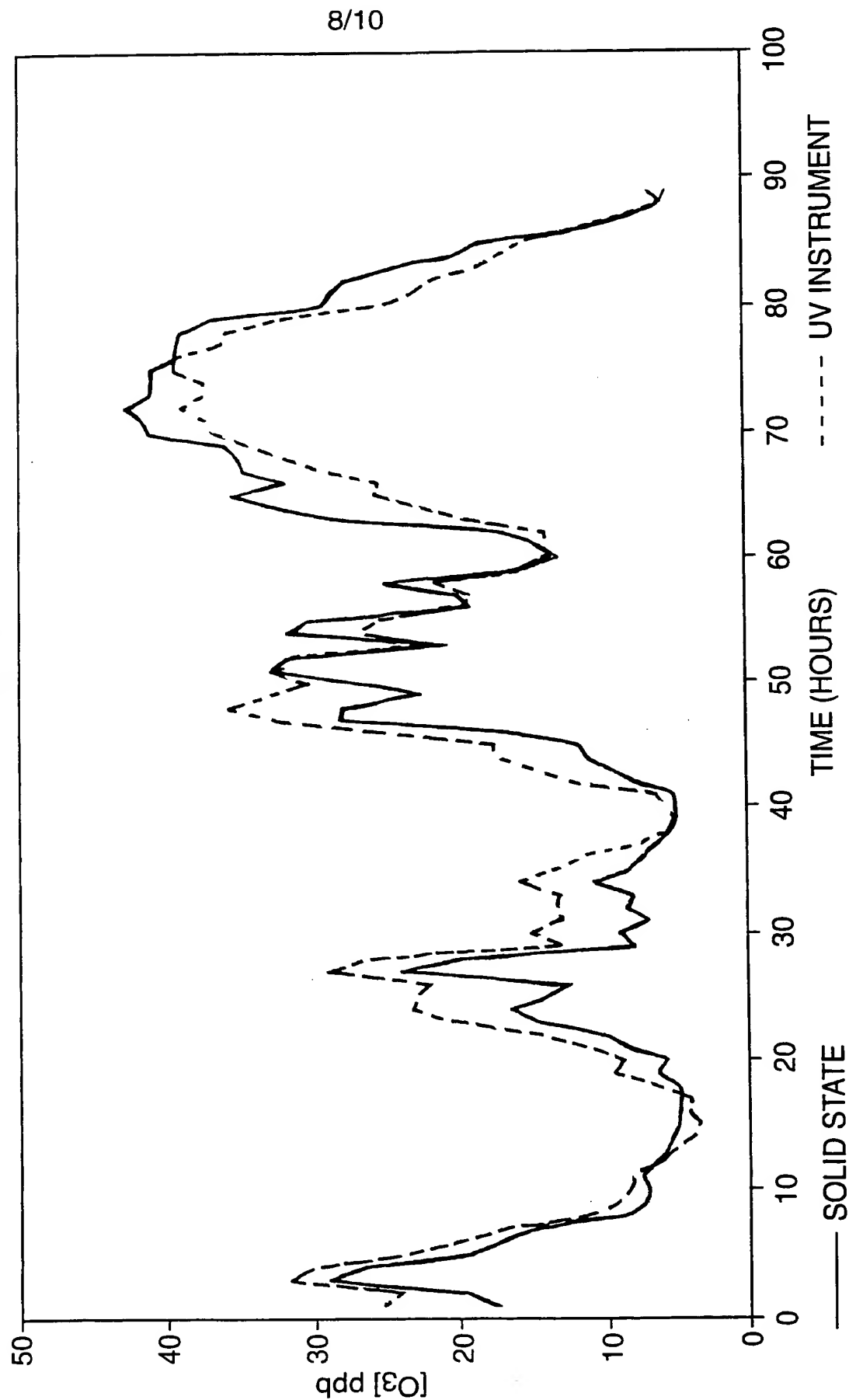


FIG. 9



9/10

FIG. 10

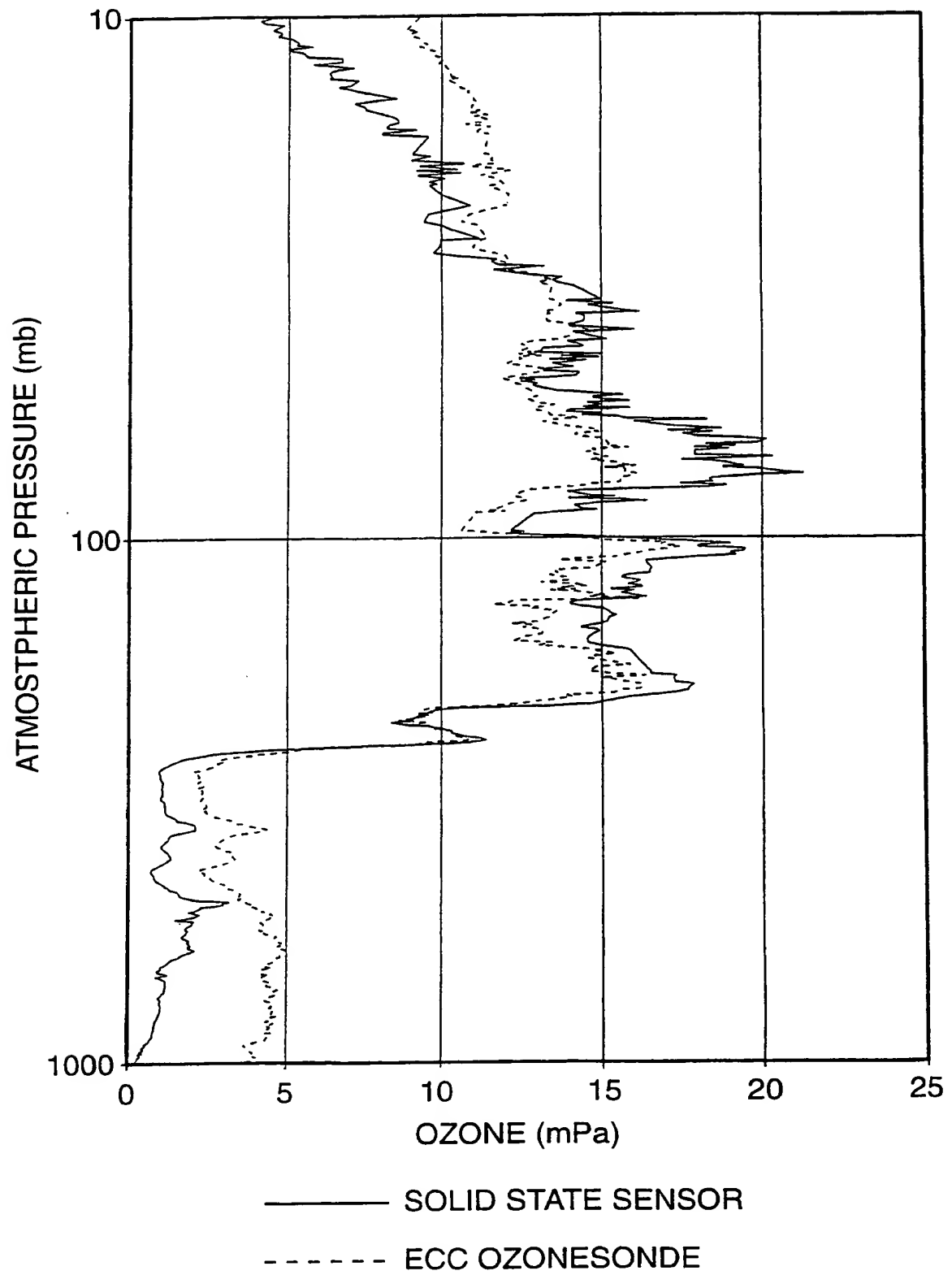
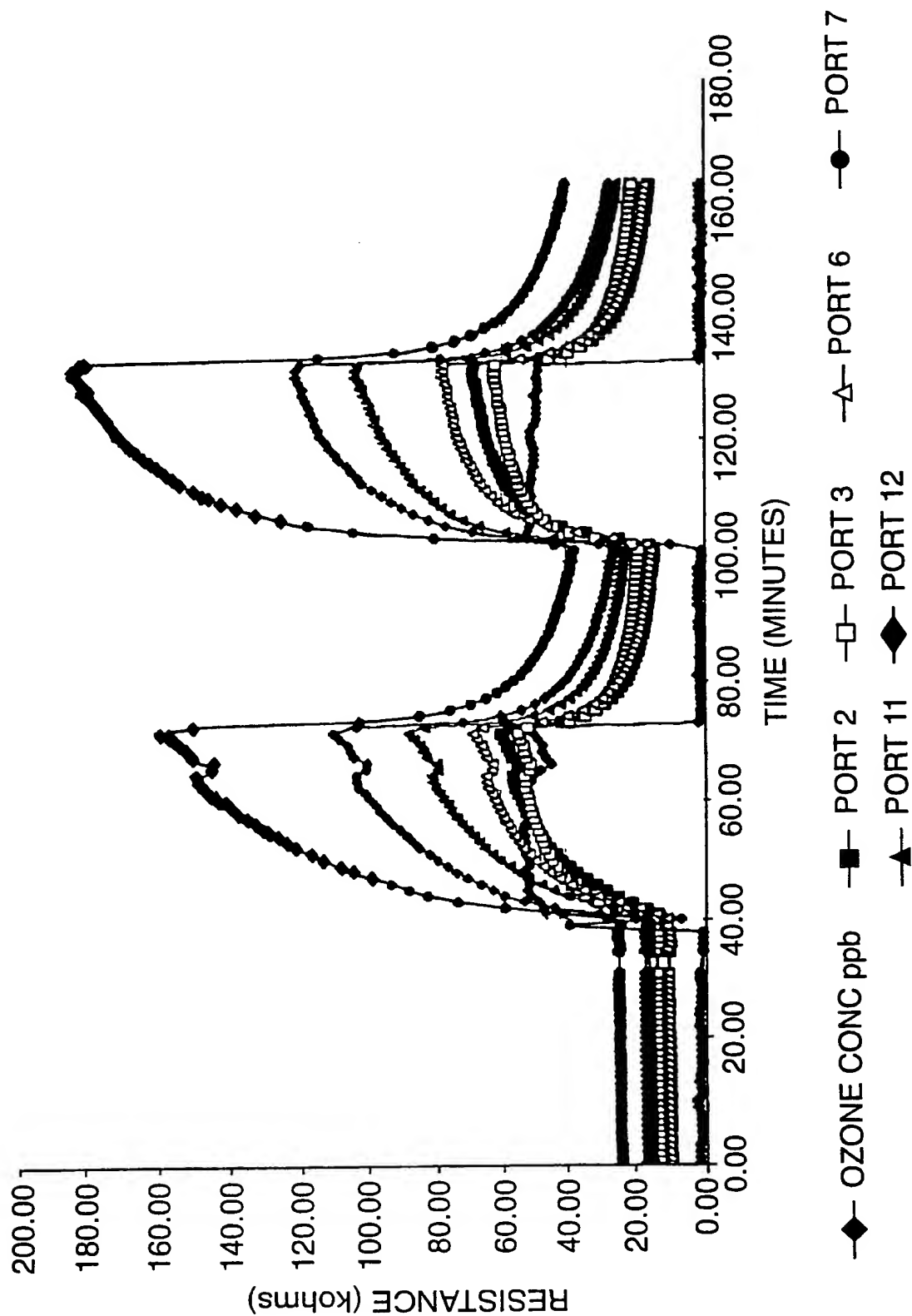


FIG. 11



PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference P019832W0	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 99/ 02757	International filing date (day/month/year) 19/08/1999	(Earliest) Priority Date (day/month/year) 03/09/1998
Applicant CAPTEUR SENSORS AND ANALYSERS LIMITED et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☒ because this figure better characterizes the invention.

11

☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

T/GB 99/02757

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G01N33/00 G01N27/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HEILIG A ET AL: "Gas identification by modulating temperatures of SnO ₂ -based thick film sensors" SENSORS AND ACTUATORS B,CH,ELSEVIER SEQUOIA S.A., LAUSANNE, vol. 43, no. 1-3, page 45-51 XP004103418 ISSN: 0925-4005	1-5, 8-10,12
Y	the whole document ---	11
X	US 4 627 269 A (FORSTER MARTIN ET AL) 9 December 1986 (1986-12-09) column 13, line 53 -column 14, line 47; figure 2 ---	6,7
Y	WO 95 35495 A (CAPTEUR SENSORS & ANALYSERS ;WILLIAMS DAVID EDWARD (GB); MOSELEY P) 28 December 1995 (1995-12-28) the whole document ---	11
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

22 December 1999

Date of mailing of the international search report

12/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bosma, R

INTERNATIONAL SEARCH REPORT

International Application No

T/GB 99/02757

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 775 912 A (ITVI INTTECH VENTURE INVESTA) 28 May 1997 (1997-05-28) the whole document ----	1-12
A	DE 43 16 970 C (DAIMLER BENZ AG) 25 August 1994 (1994-08-25) -----	1,6,7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

T/GB 99/02757

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4627269	A	09-12-1986	CH 668648 A	13-01-1989
			EP 0157237 A	09-10-1985
			ES 542648 A	16-06-1986
			JP 60228950 A	14-11-1985
<hr/>				
WO 9535495	A	28-12-1995	AU 6976594 A	17-01-1995
			CA 2193646 A	28-12-1995
			EP 0656111 A	07-06-1995
			EP 0767905 A	16-04-1997
			GB 2285689 A	19-07-1995
			GB 2305730 A, B	16-04-1997
			JP 10501623 T	10-02-1998
			JP 8500447 T	16-01-1996
			US 5811662 A	22-09-1998
<hr/>				
EP 0775912	A	28-05-1997	DE 19543296 A	22-05-1997
			CN 1165953 A	26-11-1997
			JP 9264591 A	07-10-1997
<hr/>				
DE 4316970	C	25-08-1994	NONE	
<hr/>				